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PHOSPHATE FIXATION IN SOILS, PARTICULARLY AS INFLUENCED BY ORGANIC MATTER[1]

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Although soil organic matter-phosphate relationships have received much attention, a review of the literature reveals the existence of very little definite information regarding the influence of soil organic matter on the fixation of phosphate in difficultly available form. A study of this latter phase of the subject was therefore undertaken covering the following points: (*a*) the effect of leaching a soil with an acid or a base on its fixing power; (*b*) the fixation of phosphate by natural and synthetic humus material; (*c*) the effect of oxidizing the organic matter with hydrogen peroxide or by ignition on its fixing power; (*d*) the effect of heat on the solubility of iron and aluminum phosphates in 0.002 *N* H_2SO_4.

METHODS AND MATERIALS

In this report the term "fixed phosphorus" is used to designate that portion of the applied water-soluble phosphate which is not recovered by extracting 1 gm. of soil with 200 cc. of 0.002 *N* H_2SO_4 buffered to pH 3 with $(NH_4)_2SO_4$. This is the extracting solution used by Truog (13) for the determination of readily available phosphorus and will be referred to as the "standard extracting solution."

The fixing power of the different materials was determined as follows: Weighed samples were placed in evaporating dishes and moistened with water, and the desired amount of monobasic potassium phosphate was added in solution. After drying on the steam bath, the samples were transferred to bottles and the standard extracting solution was added. The suspensions were shaken for 30 minutes on an end-over-end shaker and then filtered. Filtrates colored with organic matter were evaporated with magnesium nitrate and the residue ignited before the phosphorus was determined.

All phosphorus determinations were made by the Denigès colorimetric method as outlined by Truog and Meyer (14). The amount of phosphorus

[1] Part of a thesis submitted to the faculty of the University of Wisconsin in partial fulfillment of the requirements for the degree of doctor of philosophy. Published with the permission of the director of the Wisconsin Agricultural Experiment Station.

[2] The writer wishes to express his appreciation for the advice and criticisms tendered by Prof. E. Truog.

fixed was computed by subtracting the amount extracted from the treated sample from the sum of what was added to and originally present in soluble form in the sample. Phosphorus is reported in all cases as parts per million on the basis of the weight of the original dry sample. Iron was determined by the thiocyanate colorimetric method as given by Scott (11), and the pH determinations were made colorimetrically or by use of a quinhydrone electrode.

The following soils were used: black peat, organic matter in an advanced stage of decomposition; brown peat, organic matter partially decomposed; Edmonton loam, a mineral soil, high in organic matter; and Superior clay, a soil low in organic matter.

EFFECT OF LEACHING SOILS WITH ACID ON THEIR PHOSPHATE-FIXING POWER

The effect of leaching black peat with HCl solutions of different normalities on the phosphate-fixing power was determined as follows: Ten grams of peat were placed in a bottle with 250 cc. of the leaching solution and shaken for 30 minutes. The suspension was filtered, and the peat on the filter was leached first with an additional 250 cc. of the acid solution and then with water till free of chlorides. The fixing power of the leached material after being dried and pulverized was determined as previously outlined, and the results are given in table 1. These data show that leaching caused a depression in the phosphate-fixing power, the extent depending on the normality of the acid used. The original material fixed 45 to 72 per cent of the amount applied, but leaching with 0.05 *N* HCl reduced this to about 30 per cent. The material leached with 0.1 *N* acid fixed only 11 to 22 per cent of the applied phosphate, and that leached with *N* acid lost practically all fixing power. Normal HCl exerted considerable solvent action on the mineral fraction but not on the organic matter, indicating that the loss of fixing power was connected with the mineral material.

Further evidence regarding this loss of fixing power was obtained by determining the fixing power of the substances in the *N* HCl leachate. Aliquots of the leachate were measured out, the desired amount of phosphate was added, the solutions were evaporated, and the residues were extracted with the standard extracting solution. In a second set of aliquots, the iron and aluminum were precipitated with NH_4OH and separated by filtration. These hydroxides were then dissolved in dilute HCl, and the fixing power of the solutions was determined as with the original leachates. The data from these experiments, reported in table 2, show that the substances dissolved by the *N* HCl have fixed approximately all of the added phosphate, indicating even greater fixing power than the unleached peat (table 1). The data also show that the iron or the aluminum, or both, must be the active material in the fixation, for when separated from the extract and tested, it caused the fixation of as much phosphate as the original extract. The standard extracting solution undoubtedly had considerable solvent effect on any aluminum phosphate that was formed (12), but only slight solvent effect on the iron phosphate,

whose point of minimum solubility is approximately pH 3 (6). These results are in keeping with previous work on the fixation of phosphate by peat (3).

Since ferric iron does not ordinarily function as an exchangeable base, the fixation was probably not caused by exchangeable iron. Additional evidence that the fixing material did not exist in exchangeable form was obtained by leaching some peat with *N* KCl in the same manner as with HCl. The results,

TABLE 1

Phosphorus fixed by black peat before and after leaching with HCl and KCl

P.P.M. PHOSPHORUS ADDED, BASED ON WEIGHT OF SAMPLE	P.P.M. PHOSPHORUS FIXED BY PEAT, BASED ON WEIGHT OF ORIGINAL SAMPLE				
	Unleached	Leached with 0.05 *N* HCl	Leached with 0.1 *N* HCl	Leached with *N* HCl	Leached with *N* KCl
50	36	17	11	6	29
100	67	30	22	−2	58
200	112	68	42	−4	104
500	227	160	54	14	234

TABLE 2

Phosphorus fixed by the substances in the N *HCl extract of black peat*

P.P.M. PHOSPHORUS ADDED, BASED ON WEIGHT OF SOIL EXTRACTED	P.P.M. PHOSPHORUS FIXED, BASED ON WEIGHT OF SOIL EXTRACTED	
	By residue of HCl extract	By Fe and Al in HCl extract
50	50	48
100	92	97
200	190	192
400	387	382

TABLE 3

Phosphorus fixed by different soils before and after leaching with N *HCl*

P.P.M. PHOSPHORUS ADDED, BASED ON WEIGHT OF SAMPLE	P.P.M. PHOSPHORUS FIXED, BASED ON WEIGHT OF ORIGINAL SAMPLE					
	By brown peat		By Edmonton loam		By superior clay	
	Before leaching	After leaching	Before leaching	After leaching	Before leaching	After leaching
50	33	0	34	14	28	16
100	81	0	55	32	62	31
200	130	0	83	46	106	41

reported in table 1, and show that saturation of the exchange complex with potassium did not decrease the fixing power.

In order to determine whether the results obtained with black peat might apply generally, brown peat, Edmonton loam, and Superior clay were tested for fixing power before and after being leached with *N* HCl. Brown peat, like the black, lost its fixing power, and Edmonton loam and Superior clay lost about 50 per cent. The results are reported in table 3.

The leachate from the HCl extraction of the Superior clay was used for a subsequent series of experiments. In one series the fixing power of the residue of the leachate was determined as with the leachate from the peat. In a second series, the iron and aluminum in the leachate were separated from the other cations by precipitation with NH_4OH. The fixing power of the precipitated iron and aluminum hydroxides and of the residue of the leachate after removal of the iron and aluminum was tested in the regular way. Results are reported in table 4. These data show that the fixation by the residue of the leachate is due almost entirely to the iron and aluminum compounds present. The fixing power of the original soil was less than that of the HCl extract, although this soil did not lose all of its fixing power when leached (table 3). Apparently the fixing material became more reactive after solution and re-

TABLE 4

Phosphorus fixed by the substances in the N *HCl extract of superior clay*

P.P.M. PHOSPHORUS ADDED, BASED ON WEIGHT OF SOIL EXTRACTED	P.P.M. PHOSPHORUS FIXED, BASED ON WEIGHT OF SOIL EXTRACTED		
	By residue of HCl extract	By Fe and Al ppt. from HCl extract	By residue of HCl extract after removal of Fe and Al
50	50	47	..
100	94	94	5
200	190	188	13
400	386	378	1

TABLE 5

Phosphorus fixed by black peat after leaching with NaOH and NH_4OH

P.P.M. PHOSPHORUS ADDED, BASED ON WEIGHT OF SAMPLE	P.P.M. PHOSPHORUS FIXED BY PEAT, BASED ON WEIGHT OF ORIGINAL SAMPLE		
	Unleached	Leached with 0.05 *N* NaOH	Leached with 0.5 *N* NH_4OH
50	36	47	43
100	67	88	81
200	112	148	132
500	227	395	...

precipitation. Iron may also have been brought into solution by the HCl from rather unreactive minerals. It is to be noted that Ford (5) attributes the fixation of phosphate in difficultly available form largely to the action of hydrated iron oxide, forming basic iron phosphate.

EFFECT OF LEACHING BLACK PEAT WITH A BASE ON ITS FIXING POWER

A sample of black peat was leached with 0.05 *N* NaOH, washed with water until the filtrate gave no color with phenolphthalein, and then dried. A second sample was similarly leached with 0.5 *N* NH_4OH and washed. The fixing power of the peat after these leachings is given in table 5; a comparison with the unleached samples shows that the fixing power has been increased. Leaching a soil with an alkaline solution tends to hydrolyze any iron phosphate

present, the iron remaining as the hydroxide and the phosphate leaching out. This increases the amount of free iron oxide in the soil and accounts for the increased fixing power.

These results are in accord with those of Russell and Prescott (10) who report that the removal of the humus material from a soil by leaching with NaOH did not destroy the power of the soil to fix phosphate. There is some evidence that the alkaline leachate of a soil contains phosphorus and iron in organic combination, for they are retained by the colloidal precipitate repeatedly formed by alternate precipitation with acid and solution with alkali.

FIXATION OF PHOSPHATE BY NATURAL AND SYNTHETIC HUMUS

Purified natural humus was prepared as follows: Forty grams of peat was shaken with 1 liter of 2 *N* NaOH for 30 minutes, and part of the liquid was decanted after settling. The suspension was repeatedly made up to 1 liter with water, shaken, and decanted after settling, until approximately 2 liters of

TABLE 6

Phosphorus fixed by purified humus material extracted from peat by leaching with NaOH

PHOSPHORUS AND COAGULANTS ADDED TO NaOH HUMUS SOLUTION	PHOSPHORUS		
	In solution	Extracted from precipitate by 0.002 *N* H_2SO_4	Total soluble
	mgm.	*mgm.*	*mgm.*
Check, coagulated with HCl	0.039	None	0.039
0.01 mgm. P added, coagulated with HCl	0.050	None	0.050
Check, coagulated with $CaCl_2$	0.022	0.011	0.033
0.01 mgm. P added, coagulated with $CaCl_2$	0.023	0.020	0.043

solution were obtained. This solution was filtered through paper pulp, and the humus purified by three alternate precipitations with HCl and re-solutions in alkali, after which it was dried and pulverized. A weighed amount of the humus was dissolved in a solution of NaOH. To aliquots of the humus solution, a known amount of phosphate and then HCl or $CaCl_2$ were added until the organic matter was coagulated. After filtering, the precipitates were washed with water, dried, and then extracted with the standard extracting solution. The phosphorus contents of these extracts and of the filtrates obtained after coagulation were determined, and the results are reported in table 6. These data show that coagulation of the organic matter with HCl did not cause a precipitation of phosphate, for all the added phosphate remained in solution. Coagulating the humus with $CaCl_2$ caused a precipitation of some of the added phosphate, as shown by the increase in phosphorus extracted from the precipitate. It was precipitated, apparently, as calcium phosphate. In neither case was there any fixation in difficultly available form.

Synthetic humus was prepared as outlined by Burke, Linweaver, and

Horner (2). Fifty-gram samples of dextrose were boiled in 250 cc. of 35 per cent HCl for 15 minutes over a low flame. Fifty milligrams of iron as ferric sulfate was added to one sample of dextrose before boiling. The solutions were filtered and the precipitates dissolved with KOH and reprecipitated with HCl four times. The precipitates were dried at 105°C. and pulverized. The purified precipitates contained the following amounts of phosphorus and iron:

	Phosphorus per cent	*Iron (Fe) per cent*
Check—iron not added	0.0103	0.152
Iron added	0.0131	0.218

The dextrose used contained phosphorus and iron as shown by the check sample. The addition of iron to the solution before beating caused a marked increase in the amount of phosphorus and iron found in the precipitate.

One-half gram samples of the synthetic humus were dissolved in KOH and diluted to 200 cc. Aliquots of these solutions were measured into evaporating dishes, and 0.01 mgm. of phosphorus was added. Hydrochloric acid was added to each until coagulation of the organic material took place, which was approximately at the neutral point. After evaporation on the steam bath, the residues were extracted with 50 cc. of standard extracting solution. The added phosphate was all recovered in both series. These results are similar to those obtained with natural humus.

Experiments using finely ground alfalfa and organic base exchange material as prepared by Mitchell (8) showed that these organic substances did not possess the power to fix phosphates.

Dumont (4) found that humus soil containing varying amounts of lime fixed more monocalcium phosphate than did mineral soils. This, however, is not fixation in difficultly available form. Bottini (1) advanced the theory of the formation of humo-phosphates, which are mixtures of calcium humate and calcium phosphate. These humo-phosphates are supposed to be formed only under neutral or alkaline conditions. Evidence of the formation of similar compounds was obtained in the present investigation when natural humus material was treated with phosphate and calcium chloride.

EFFECT OF OXIDATION WITH HYDROGEN PEROXIDE ON THE FIXING POWER OF BLACK PEAT

Hydrogen peroxide (approximately 30 per cent) was freed of phosphate by distilling under vacuum and collecting the distillate in a flask packed in ice. The strength is usually reduced somewhat by this distillation.

The black peat was oxidized by adding a small quantity of the purified hydrogen peroxide to the wet sample and heating on the steam bath until bubbling had practically ceased. This treatment was repeated until the desired degree of oxidation was obtained. The resulting suspension was then boiled for a few minutes, filtered, and the residue washed with hot water until it became practically free of soluble organic matter. The residue was dried, weighed, and then pulverized.

The fixing power of fractions of the residue equivalent to 1 gm. of the original peat was determined in the usual manner. Aliquots of the water filtrates and washings were also used for fixation tests. The results of these experiments are reported in table 7. These data show that the treatment with hydrogen peroxide has reduced the fixation of added phosphate from 157 p.p.m. in the untreated sample to 5 p.p.m. in the sample treated with 4 cc. of hydrogen peroxide per gram of soil. This reduction in fixing power is attributed to a partial saturation of the fixing material with the phosphate liberated from the organic matter during oxidation. The acidity developed in the solutions during oxidation was approximately pH 4, which would still permit the formation of ferric phosphate.

The substances in the water extracts and washings showed some fixing power, but not enough to account for the loss in the corresponding residues. There was a gradual increase in the amount of phosphorus fixed by the substances in the water extracts with increased oxidation. The increased oxida-

TABLE 7

Phosphorus fixed by the residue and by the substances in the water extract of black peat after oxidation with hydrogen peroxide

H_2O_2 ADDED PER GM. PEAT	P.P.M. PHOSPHORUS ADDED, BASED ON WEIGHT OF ORIGINAL SAMPLE	P.P.M. PHOSPHORUS FIXED, BASED ON WEIGHT OF SAMPLE TREATED	
		By residue of water extract	By substances in water extract
cc.			
0	200	157	..
1	200	58	33
2	200	29	46
3	200	11	45
4	200	5	68

tion probably raised the amount of free ferric iron in the extracts, which would account for the greater fixation.

The oxidation of the peat brought large amounts of phosphorus and iron into solution. It was found that the water-soluble phosphorus increased from 15 p.p.m. when the soil was untreated to 334 p.p.m. when 4 cc. of hydrogen peroxide was used. Further oxidation, using as high as 30 cc. per gram of soil, caused only a slight additional increase. The water-soluble iron increased from 96 p.p.m. in the untreated to 4,960 p.p.m. when the peat was treated with 4 cc. of hydrogen peroxide per gram. At greater oxidation there was a still further increase.

These results are more or less in keeping with the work of Peterson (9), who found that approximately a maximum amount of phosphorus was made soluble in 0.2 *N* HNO_3 by the time one-third of the organic matter had been oxidized. He also found that the increase in soluble iron was roughly parallel, though not proportional, to the increase in soluble phosphorus.

The large amounts of iron in the water extracts following the hydrogen peroxide treatments should fix much more phosphate than is shown in table 7. Attempts to throw this iron out of solution with NH_4OH were unsuccessful, indicating that it must be held in combination with or protected by the organic matter, for if present in an inorganic form, it would have been precipitated.

The organic matter in a highly colored water extract of a peroxide-treated peat was destroyed by taking to dryness in the presence of hydrogen peroxide and then adding H_2SO_4 and igniting. The residue was taken up in HCl, the iron precipitated with NH_4OH, and the precipitate washed and then dissolved in HCl. Aliquots of this solution were used for an iron determination and for fixation experiments. When phosphorus was added at the rate of 200 p.p.m., 190 p.p.m. were fixed. Since the extract contained approximately 3,000 p.p.m. of iron, the maximum fixing power possible was probably much higher than that indicated. The fixation was much greater than when the iron was combined with the organic matter (table 7).

Five peats were subjected to five successive oxidations with hydrogen peroxide to determine whether there exists a definite iron-phosphorus ratio in the material dissolved. The samples were washed free of soluble organic matter after each peroxide treatment. No definite iron-phosphorus ratio was found in the water-soluble material.

Samples of Goethite ($Fe_2O_3 \cdot H_2O$), peat ash, and aliquots of an acid extract of peat were treated with hydrogen peroxide to determine the effect on their fixing power. In no case was there any apparent reduction in the fixing power.

EFFECT OF HEAT ON THE FIXING POWER OF BLACK PEAT AND GOETHITE

Samples of black peat and Goethite were heated for 2 hours at temperatures of 200°, 400°, 600°, and 800°C. in an electric furnace, and their fixing power was determined thereafter. Heating for 2 hours at 400°C. destroyed all organic matter. Because of the alkalinity of the peat ash, varying amounts of acid had to be added to the extracting solution to maintain the desired acidity, pH 3. The residues of the peat samples which had been heated at 800°C. were not so alkaline as those heated at 600°C., requiring only one-half as much acid to maintain a pH of 3. Reaction and combination of the bases with silica at the higher temperatures may have caused this.

The data in table 8 show that heating the peat at 200°C. for 2 hours caused a depression in its fixing power and an increase in soluble phosphorus. Ford (5) found that heating certain mineral soils at 210°C. for 13 days decreased their fixing power. He attributed the decrease to a dehydration of the Goethite which they supposedly contained. In table 8 it is found that heating Goethite for only 2 hours at 200°C. did not appreciably decrease its fixing power, but at higher temperatures there was a decided decrease. The residue of the peat heated at 400°C. had a slightly greater fixing power than the unheated peat. A further increase resulted at 600°C. The residues of the samples heated at

800°C. would not fix phosphate, probably because of the inactivation of the iron oxide.

The amount of soluble phosphorus in the peat residue increased from 12 to 304 p.p.m. when the temperature of heating was raised from 600° to 800°C. (table 8). This increase was probably caused by a breaking down of the ferric phosphates and the formation of ferric oxide and calcium phosphate. Similar results were obtained when mixtures of ferric phosphate and CaO were heated to 800°C.

Mitchell (8) found that heating a soil at 350°C. destroyed the organic base exchange complex. Since heating black peat at 400°C. for 2 hours did not reduce the fixing power (table 8), it appears that the organic base exchange complex does not enter into phosphate fixation.

TABLE 8

Phosphorus soluble and fixed by black peat and Goethite before and after heating for 2 hours at various temperatures

P.P.M. PHOSPHORUS ADDED, BASED ON WEIGHT ORIGINAL SAMPLE	P.P.M. PHOSPHORUS SOLUBLE IN 0.002 *N* H_2SO_4 AND FIXED AFTER TREATMENTS INDICATED, BASED ON WEIGHT OF ORIGINAL SAMPLE									
	Check, unheated		Heated at 200°C.		Heated at 400°C.		Heated at 600°C.		Heated at 800°C.	
	Soluble	Fixed	Soluble	Fixed	Soluble	Fixed	Soluble	Fixed	Soluble	Fixed
					Peat					
None	21	...	86	...	26	...	12	...	304	..
50	35	36	112	24	33	43	19	41	352	2
100	54	67	134	52	66	60	22	90	376	28
200	109	112	176	110	72	154	30	180	494	10
					Geothite					
None	None	...	None	...	9	...	26	...	84	..
100	2	98	3	97	31	78	59	67	184	None

Kelley, Dore, and Brown (7) found that the exchange capacity of the inorganic soil colloids was reduced approximately two-thirds by heating at 600°C. Heating black peat at 600°C. did not cause any loss in power to fix phosphate, showing that the fixing power was not dependent on the exchange capacity of the inorganic base exchange complex.

EFFECT OF HEAT ON THE SOLUBILITY OF PHOSPHATIC COMPOUNDS OF IRON AND ALUMINUM IN 0.002 *N* H_2SO_4

The large increase in soluble phosphorus in the residues of the peat samples heated at 800°C. indicated that the ferric phosphates were being broken down and calcium phosphate was being formed. Additional evidence on this point was obtained as follows: One-tenth-gram samples of ordinary C.P. precipitated

iron and aluminum phosphates were heated in an electric furnace at various temperatures and then extracted with 100 cc. of the standard extracting solution. To a set of duplicate samples, 0.06 gm. of CaO was added before heating. The samples were placed in the cold furnace and removed when the desired temperature was reached. Sufficient H_2SO_4 was added to the extracting solution to neutralize the CaO and maintain the solution at pH 3. The samples were heated in Sillimanite crucibles to prevent a reaction between the crucible and sample at the higher temperatures.

The data in table 9 show that heating the ferric phosphate alone at 800°C. decreased the soluble phosphorus from 0.138 mgm. to 0.072 mgm. The decrease is attributed to a dehydration of the ferric phosphate at the higher temperatures, though part of the effect may be due to a slight change in physical condition, thus reducing the surface exposed. The increased solubility of phosphorus when the ferric phosphate was heated with CaO is probably

TABLE 9

Phosphorus dissolved from 0.1-gm. samples of $FePO_4$ and $AlPO_4$ by 0.002 N H_2SO_4, before and after being heated alone and with CaO

TEMPERATURE OF HEATING	PHOSPHORUS DISSOLVED BY 0.002 *N* H_2SO_4 BEFORE AND AFTER HEATING OF MATERIALS INDICATED			
	$FePO_4$	$FePO_4$ + CaO	$AlPO_4$	$AlPO_4$ + CaO
°C.	*mgm.*	*mgm.*	*mgm.*	*mgm.*
Unheated	0.138	0.131	0.90	1.09
200	0.148	0.143	1.36	1.79
400	0.152	0.164	.....	.....
500	.....	.....	0.86	1.49
600	0.116	0.915	0.03	0.195
700	0.092	1.78	.....	.....
800	0.072	2.58	0.012	0.545

caused by a breaking down of the ferric phosphate and the formation of ferric oxide and calcium phosphate. This reaction began at approximately 600°C., although a greater recovery of phosphate was obtained by heating to 800°C.

Four samples of natural hydrated iron oxides containing some phosphorus, probably as basic ferric phosphate, showed a large increase in phosphorus soluble in 0.002 *N* H_2SO_4 when heated to 800°C.

When the $AlPO_4$ was heated to 200°C. the soluble phosphorus increased; when it was heated to 500°C., the soluble phosphorus was about the same in amount as for the unheated material; but at 600° and 800°C., the soluble phosphorus was greatly decreased. At 500°C. the $AlPO_4$ showed a slight tendency to fuse, and at 600°C. and over, it fused into hard lumps. The decreased solubility may have been due to the decreased surface, although pulverizing in an agate mortar did not increase the solubility to that of the original material. If the same degree of fineness as that of the original material had been obtained, the solubility might have been the same as the original. When

CaO was mixed with the $AlPO_4$ there was a very decided decrease in soluble phosphorus after heating to 600°C. The solubility after heating to 800°C. was approximately one-half that of the unheated material, though greater than when heated to 600°C. The amount of fusion was not so great in the presence of the CaO, although there was a tendency to form hard particles at 600° and 800°C. Peterson (9) found that heating wavellite at 185° and 240°C. increased the amount of phosphorus soluble in 0.2 *N* HNO_3.

A sample of apatite gave no increase in soluble phosphorus when heated to 800°C. When the apatite was mixed with CaO and then heated to 800°C. the amount of soluble phosphorus was reduced approximately 50 per cent.

From the foregoing results it is evident that the increase in soluble phosphorus when the peat was heated at 800°C. (table 8) was caused by a breaking down of the ferric phosphates, because of reaction with lime and other bases.

SUMMARY

Experiments were conducted to determine the effect of the following treatments on the power of the organic matter of soils to fix added phosphate: (*a*) leaching with HCl; (*b*) leaching with NaOH and NH_4OH; (*c*) oxidation of the organic matter with hydrogen peroxide; (*d*) heating at temperatures up to 800°C. The fixation of phosphate by natural and synthetic humus material and the effect of heat on the solubility of two phosphatic compounds were also studied.

Leaching the soils with HCl reduced the fixing power for added phosphates. The ferric iron in the acid leachings possessed somewhat greater fixing power than the soils from which these leachings were derived.

Leaching peat with NaOH or NH_4OH increased its fixing power because of an increase in active iron. The alkaline extracts did not fix phosphates.

Natural and synthetic humus did not fix phosphate.

Oxidation of the organic material with hydrogen peroxide decreased the power of soils to fix added phosphates, the decrease being greater where the oxidation was greater. This loss of fixing power is attributed to a saturation of the fixing material with phosphorus liberated from organic compounds during oxidation.

Heating peat at 600°C. for 2 hours did not destroy its power to fix phosphate. Heating at 800°C. for 2 hours caused a complete loss of fixing power. The increase in phosphorus soluble in 0.002 *N* H_2SO_4 when peat was heated at 800°C is attributed to reaction of ferric phosphates with lime to form calcium phosphate.

Heating a mixture of ferric phosphate and CaO to 800°C. caused a large increase in phosphorus soluble in 0.002 *N* H_2SO_4. When $AlPO_4$ was heated under the same conditions there was less soluble phosphorus than in the unheated material.

The evidence shows that soil organic matter as such has only a minor rôle, if any, in the fixation of phosphorus in difficultly available form when soluble phosphatic fertilizers are applied to a soil.

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FLUORINE, ITS EFFECT ON PLANT GROWTH AND ITS RELATION TO THE AVAILABILITY TO PLANTS OF PHOSPHORUS IN PHOSPHATE ROCKS[1]

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Fluorine occurs naturally in phosphate rocks (10) which are used in the manufacture of superphosphates and is also found in the manufactured product in amounts varying from about 1 to 3 per cent.[3] The addition of these compounds to the soil incorporates appreciable quantities of fluorine in the soil. The use of fluorides and fluosilicates as insecticides will also add fluorine to soils. Fluorine compounds have been reported to increase plant growth under certain conditions and to decrease it under others. Gautier and Clausman (9) report that the application of 100 p.p.m. of fluorine as calcium fluoride to field plots definitely increased the yield of some plots. Mazé (11) states that fluorine is indispensable for the growth of corn. Aso (1, 2) found differences in the effect of sodium fluoride and sodium silico-fluoride on the growth of plants in solution cultures. Some plants were able to develop normally in concentrations of 0.001 per cent, whereas others were killed at that concentration. Greater concentrations than 0.001 per cent of either salt were injurious to all plants used. Wilson (13) and Wöber (14) report that fluorine has a toxic effect on the development of certain plants. With such divergent results from the few experiments reported, more information on the effect of fluorine on plant growth is desirable.

Fluorine could affect the growth of plants in several ways. The results in this report are concerned with the effect of fluorine on the germination of seeds, the production of dry matter by plants, and the availability of phosphorus from various phosphates.

EFFECT OF FLUORINE ON GERMINATION

Sudan grass, cowpea, soybean, red clover, and white Dutch clover seeds were germinated according to the official method of the State Seed Laboratory, modified so that solutions containing known amounts of fluorine as sodium or

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calcium fluoride were used instead of water in wetting the germination pads. The largest concentration of fluorine used is greater than would be added to soils in heavy applications of known phosphates. The results are given in table 1.

The results with Sudan grass are nearly all lower when fluoride solutions are used in wetting the germination pads. The differences, with the exception of 1 p.p.m. of fluorine as sodium fluoride and 3 p.p.m. as calcium fluoride are

TABLE 1

Effect of varying concentrations of fluorine compounds on the germination of seeds

SOURCE OF FLUORINE	CONCENTRATION OF F	VIABLE SEED					
		Sudan grass A	Sudan grass B	Cowpea	Soybean	White Dutch clover	Red clover
	p.p.m.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
None	0	83.5	89.5	79.0	91.5	31.0	66.0
NaF	0.25	77.0	....	79.0	93.5	29.5	64.5
NaF	0.50	79.0	....	77.5	86.5	31.5	63.0
NaF	1.00	72.0	....	79.5	91.5	32.5	58.0
NaF	3.00	81.0	....	80.0	92.0	32.0	59.5
NaF	5.00	77.0	....	78.0	91.5	32.0	59.5
NaF	10.00	....	85.5	....	90.0	39.0	61.5
NaF	50.00	....	89.5	....	84.0	35.5	61.5
CaF_2	0.25	80.0	....	80.0	91.5	42.5	58.5
CaF_2	0.50	81.5	....	83.5	92.5	45.5	58.5
CaF_2	1.00	80.0	....	81.5	91.0	39.5	60.5
CaF_2	3.00	71.5	....	80.0	90.0	42.0	65.0
CaF_2	5.00	80.0	....	75.5	89.5	43.0	62.0
CaF_2	7.72	....	....	....	89.5	52.5	56.5
Na_2SiF_6	0.25	....	88.0	....	89.5	39.0	68.0
Na_2SiF_6	0.50	....	88.5	....	91.5	47.5	54.0
Na_2SiF_6	1.00	....	87.5	....	91.5	50.0	60.0
Na_2SiF_6	3.00	....	89.5	....	88.5	48.0	55.5
Na_2SiF_6	5.00	....	91.0	....	91.0	49.0	63.5
Na_2SiF_6	10.00	....	88.5	....	94.0	45.5	58.0
Na_2SiF_6	50.00	....	87.0	....	91.5	50.0	59.5

within the limits of error allowed in germination tests. The results from the cowpeas and soybeans show no injurious effect on the germination of these seeds. Although the red clover and white Dutch clover were old seeds the results give little evidence of decreased germinations because of the fluorine added. The results with red clover excepting the 0.5 and 3.0 p.p.m. of fluorine as sodium fluosilicate are within the limits of error allowed. The use of fluorine as calcium fluoride and sodium fluosilicate increased the percentage of germination from white Dutch clover. The results all show

that fluorine as sodium or calcium fluoride and sodium fluosilicate had little, if any, injurious effect on the germination of the seeds used.

EFFECT OF FLUORINE ON THE PRODUCTION OF DRY MATTER

Several experiments using cowpeas as the test crop were conducted in solution cultures similar to those previously reported (4). The seedlings were transferred from sand to the culture solution when the first leaves were formed and were permitted to grow for 10 days before the fluorine treatments were given. One plant was grown per jar in the first series, four in the second series, and three in the last series. In 1932 the fluorine compounds were added directly to the culture solutions, whereas in the other series separate jars were used for the fluorine compounds and the plants were permitted to grow for alternate periods in each solution. In the second series the fluorine solutions were renewed weekly, and after it was found that, because of absorption of fluorine in varying amounts by the plants, the initial concentrations of fluorine were not being maintained, the crop was harvested and the third series started. In this series the fluorine solutions were renewed daily. Iron was given as needed by placing the plants for several hours in an iron citrate solution having a pH of 4. Sodium fluoride was used as the standard fluorine treatment, and calcium fluoride and sodium fluosilicate were used as supplementary treatments. The concentrations of fluorine used were selected as being comparable to those which might develop in the soil solution after fluorine-bearing compounds were added to the soil. The plants in the first series were permitted to grow almost twice as long as the third series.

There were slight reductions in the amount of dry matter produced where fluorine was added in the 1932 series but in most cases they were less than 12 per cent, usually about 5 per cent, and could be attributed to plant variation or experimental error (table 2).

It should be mentioned that in the second series not only were the plants in different jars depleting the concentration of fluorine at different rates, as determined by analyses of the culture solutions, but great differences in appearance existed in the plants on duplicate jars. Prior to the time of harvesting, small areas in the center of the leaves had died and in some cases the dead areas spread to include the whole leaf. Microscopical examination revealed bacteria in cross-sections of the stems but not in any of the leaf areas. Although the dead spots in the leaves may have been due to the bacterial infection and not to the presence of fluorine, the appearance did not indicate that such was the case. However, there was no way of determining whether the injury was caused by the presence of fluorine.

In the third series where the concentrations of fluorine were maintained as nearly constant as possible, the results are decidedly variable. In general the results agree with those from the other two series in showing very little decrease in dry weight which can be attributed to the presence of fluorine. For example the dry weight of the plants where 3 p.p.m. of fluorine was added

as sodium fluoride was only 8.5 gm. as compared to 18.5 gm. for the check and 18.6 gm. where 5 p.p.m. of fluorine was added. This decrease was undoubtedly caused by plant variation.

The results from the three series as a whole indicate that soluble fluorine in concentrations under 10 p.p.m. had decreased very little, if any, the amounts of dry matter produced by cowpeas growing in solution cultures.

FLUORINE AND PHOSPHORUS CONTENT OF PLANTS

The roots and tops were ground and analyzed separately for fluorine and phosphorus. The fluorine was distilled from the plant tissue after the method of Willard and Winter (12) and either titrated according to that method or

TABLE 2

Dry weight of cowpeas grown in nutrient solution with the concentration of fluorine indicated

SOURCE OF FLUORINE	CONCENTRATION OF FLUORINE	1932	1933-A	1933-B	
		Average dry weight one plant	Average dry weight four plants	Average dry weight three plants	
				Tops	Roots
	p.p.m.	*gm.*	*gm.*	*gm.*	*gm.*
None	0	17.7	8.3	18.5	9.2
NaF	0.25	15.5	6.6	21.2	9.5
NaF	0.50	16.7	9.4	21.6	10.9
NaF	1.00	13.9	7.3	33.2	16.7
NaF	3.00	13.0	8.8	8.5	5.5
NaF	5.00	17.9	9.9	18.6	9.8
NaF	10.00	15.4	10.2	10.9	6.8
CaF_2	0.25	18.5	8.4	13.3	9.3
CaF_2	0.50	15.8	7.0	24.9	11.8
CaF_2	7.72	16.7	5.5	17.2	9.4
Na_2SiF_6	0.25	15.1	15.3	21.3	12.6
Na_2SiF_6	0.50	13.2	7.3	19.2	11.1
Na_2SiF_6	1.00	16.6	7.0	12.5	7.6
Na_2SiF_6	10.00	16.3	1.9	15.6	7.5

determined colorimetrically by the Foster method (7). Phosphorus was determined volumetrically in a nitric acid extract of the residue from a magnesium nitrate fusion. The result of duplicate analyses on duplicate treatments are given in table 3.

The results show that fluorine may be absorbed in appreciable quantities by plants, particularly when the concentration of fluorine in solution is relatively high. It is of especial importance to note that most of the fluorine was found in the roots of the plants and that with one exception the roots also contained a higher percentage of phosphorus than the tops of the Sudan grass. This is in agreement with the results reported by Gautier and Clausman (8). On the contrary, however, as the fluorine content of the tops increases,

TABLE 3

Phosphorus and fluorine content of cowpeas grown in complete nutrient solution and fluorine-containing solutions as indicated

SOURCE OF FLUORINE	CONCENTRATION OF FLUORINE	ROOTS		TOPS	
		P	F	P	F
	p.p.m.	*per cent*	*p.p.m.*	*per cent*	*p.p.m.*
None	0	0.200	0.0	0.148	0.0
		0.218	0.0	0.153	0.0
NaF	0.25	0.213	13.7	0.135	0.0
		0.185	58.0	0.167	0.0
NaF	0.50	0.240	13.7	0.153	0.0
		0.223	8.0	0.125	0.0
NaF	1.00	0.223	60.0	0.102	0.0
		0.220	39.1	0.125	0.0
NaF	3.00	0.248	237.5	0.125	0.0
		0.298	550.0	0.180	8.0
NaF	5.00	0.195	838.0	0.110	63.7
		0.215	427.0	0.113	63.7
NaF	10.00	0.200	826.0	0.135	26.2
		0.200	1,086.0	0.118	40.0
CaF_2	0.25	0.228	0.0	0.155	0.0
		0.238	0.0	0.148	0.0
CaF_2	0.50	0.170	0.0	0.130	0.0
		0.180	0.0	0.145	0.0
CaF_2	7.72	0.215	84.3	0.248	0.0
		0.182	78.3	0.128	11.0
Na_2SiF_6	0.25	0.203	0.0	0.135	0.0
		0.155	0.0	*	*
Na_2SiF_6	0.50	0.185	0.0	0.140	0.0
		0.200	13.7	0.130	0.0
Na_2SiF_6	1.00	0.203	37.4	0.128	0.0
		0.190	42.7	0.128	0.0
Na_2SiF_6	10.00	0.193	1,970.0	0.108	415.0
		0.195	1,116.0	0.105	475.0

* Sample lost.

there is a tendency for the percentage of phosphorus to decrease. A general trend for the percentage of phosphorus in the tops to decrease as the percentage of fluorine in the roots increases is also shown. Furthermore, fluorine was found in the tops of only those plants containing large amounts of fluorine in the roots. There is, however, no specific correlation between the percentage of fluorine in the plant and the percentage of phosphorus in the plant.

When it is observed that fluorine was present in many of the roots of the plant and in only a few instances in the tops, the question may well be raised as to what prevents the fluorine from moving into the tops of the plants.

There are two possible explanations for this situation, both of which are based on the precipitation of the fluorine either inside the roots or on the surface of the roots. Experiments with solutions of K_2HPO_4, $CaH_4(PO_4)_2 \cdot H_2O$, and CaF_2 gave results which showed that after the solutions had stood for one week no precipitate was formed in solutions containing 5 p.p.m. of P as K_2HPO_4 and increasing amounts of F up to 7 p.p.m. as CaF_2. On the other hand, a slight cloudiness developed in a few hours when 5 p.p.m. F as CaF_2 was added to a solution containing 5 p.p.m. of P as $CaH_4(PO_4)_2 \cdot H_2O$. No precipitate was formed when only 3 p.p.m. F was added as CaF_2. Although the precipitate was very slight, its presence was definitely established by means of a photo-electric cell. The reduction in light intensity was equivalent to 7 microamperes when the light was passed through the solution containing the precipitate. Because of the small amount and the colloidal nature of the precipitate, a sufficient amount for analysis could not be obtained. From a theoretical consideration the precipitate was presumably some form of a calcium fluophosphate. The solubilities as given by Comey (5) for $Ca_3(PO_4)_2$ vary from 10 to 100 mgm. per liter; for CaF_2, from 14 to 16 mgm. per liter; and for fluorapatite, only 2 mgm. per liter. This assumption is substantiated in part by the results from the growth of Sudan grass in culture solutions containing fluorine. As previously stated, the greatest concentrations of fluorine and phosphorus were found in the roots and in many cases no fluorine was found in the tops, indicating that it had been precipitated from solution before it reached the tops of the plants.

A similar reaction to that described may be one of the factors preventing the efficient utilization of phosphorus in rock phosphate by crops.

AVAILABILITY OF FLUORINE-BEARING PHOSPHATES

Many studies have been made concerning the availability of rock phosphates to plants. The results of these studies have been conclusive in showing that rock phosphate was not an efficient source of phosphorus for the fertilization of many plants. Since fluorine is a constituent of most rock phosphates, experiments were started to determine whether its presence had any influence on the availability of rock phosphates for plant growth.

Cowpea plants were germinated in sand and placed in 2-liter percolators in culture solutions similar, except for phosphates, to those used in the foregoing

experiments. Equivalent amounts of phosphates, however, were placed in collodion bags, distilled water was added, and the bags were fastened so that phosphorus could get into the nutrient solution only by dialysis. The results from this experiment are given in table 4.

The results show that rock phosphate made poor growth as compared to monocalcium phosphate and precipitated tri-calcium phosphate. This will be discussed further.

Another series was conducted with cowpeas, four plants per jar, in jars containing 7.5 liters of culture solution. Phosphorus was added as monocalcium phosphate, precipitated tri-calcium phosphate, ammoniated superphosphate, rock phosphate, and fluorapatite to duplicate jars in amounts

TABLE 4

Green weight of cowpea plants grown with phosphate fertilization indicated

SOURCE OF P	AVERAGE GREEN WEIGHT PER PLANT
	gm.
$CaH_4(PO_4)_2 \cdot H_2O$	19.25
$Ca_3(PO_4)_2$	13.0
Rock phosphate (Ruhms)	4.5

TABLE 5

Dialyzed phosphorus in solution after 24- and 48-hour intervals

SOURCE OF P	CONCENTRATION OF P IN SOLUTION	
	24 hours	48 hours
	p.p.m.	*p.p.m.*
$CaH_4(PO_4)_2 \cdot H_2O$	0.0125	0.0225
$Ca_3(PO_4)_2$	0.5213	1.3900
Ammoniated superphosphate	0.3225	0.7710
Rock phosphate (Ruhms)	0.0125	0.01875
Fluorapatite	0.0100	0.01375

equivalent to 300 mgm. P_2O_5 per jar. The phosphate for each jar was divided into equal parts and placed in two collodion bags, one of which was weighted with quartz pebbles to hold it on the bottom of the jar. After the bags had been sealed as in the preceding experiment, they were placed in the culture solution. The culture solutions were maintained as 7.5 liters by the daily addition of distilled water. The solutions were renewed at the end of 4 weeks, and a fresh addition of phosphorus was made in the same manner as described.

The discarded bags containing phosphorus were each placed in a liter of distilled water, and after 24 and 48 hours aliquots were analyzed by the Deniges blue color method (6) to determine the rate at which phosphorus was being dialyzed. The results are given in table 5.

The results indicate that all of the phosphorus from monocalcium phosphate had been dialyzed but that phosphorus was still coming into solution from the other compounds although in very small amounts from rock phosphate and fluorapatite. The results for ammoniated superphosphate do not permit a differentiation between it and precipitated tri-calcium phosphate, although it will be shown later that the smaller concentration in solution was in all probability due to a slower rate of dialysis and not due to previous utilization of the phosphorus.

TABLE 6

Daily concentration of phosphorus in solution, dialyzed from the compounds indicated

SOURCE OF P	CONCENTRATION OF P ON FOLLOWING DATES IN JUNE, 1933										
	3	4	5	6	7	8	10	11	12	15	16
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
$CaH_4(PO_4)\cdot H_2O$	8.080	10.420	11.830	10.040	8.090	7.130	2.230	0.590	0.156	7.726*	6.250
Ca_3PO_4	0.031	0.169	0.045	0.049	0.044	0.021	†	0.018	0.021	0.017*	0.01
Ammoniated superphosphate	0.021	0.060	0.084	0.143	0.072	0.029	0.019	0.009	0.006	0.016*	0.015
Rock phosphate (Ruhms)	0.015	0.010	0.011	0.011	0.007	0.003	0.003	0.001	0.001	0.008*	0.002
Fluorapatite	0.012	0.006	0.014	0.014	0.011	0.002	0.004	0.002	0.002	0.002*	0.003

* Renewed phosphorus in new collodion bags.

† Beakers broke during analysis.

TABLE 7

Dry weights of cowpea plants grown with the source of phosphorus indicated and supplied by dialysis from a collodion membrane

SOURCE OF P	AVERAGE OVEN-DRY WEIGHT 4 plants	
	Tops	Roots
	gm.	*gm.*
$CaH_4(PO_4)_2\cdot H_2O$	28.7	7.1
$Ca_3(PO_4)_2$	17.1	7.3
Ammoniated superphosphate	11.0	5.1
Rock phosphate (Ruhms)	1.4	1.6
Fluorapatite	1.6	1.9

Because of the large differences already noted, analyses were made on samples of solution taken at frequent intervals from the renewed culture solutions in which the plants were growing. The results are given in table 6.

The results show that monocalcium phosphate dialyzes very readily through the collodion membrane used, whereas the other compounds move through the membrane in much smaller amounts. It is presumed that this difference is the result of differences in the solubility of the compounds, although the rate of permeability of the compounds may differ. The amounts of phosphorus

found in the solutions containing rock phosphate and fluorapatite were very small. The large decreases in concentration of phosphorus in solution after the first few days were undoubtedly caused by the increased feeding as the plants and roots increased in size.

The amounts of dry matter produced by cowpeas in these experiments are given in table 7. The results show a wide variation in the ability of the phosphates to supply the plants with phosphorus when the phosphorus has to dialyze through a collodion membrane. A similar condition may exist in soils. The colloidal material in the soil separating the roots and the soil particle may act as a membrane through which the phosphorus must be dialyzed before the plants can absorb it. Similarly, particles of solid phosphates such as rock phosphate may be covered with a thin layer of colloidal matter which may act as a dialyzing membrane.

To study further the availability of rock phosphate another experiment was started in culture solutions in which equivalent amounts of phosphorus as monocalcium phosphate and rock phosphate in collodion bags were compared

TABLE 8

Dry weights of cowpea plants grown as described

SOURCE OF P	AVERAGE DRY WEIGHT OF PLANTS	
	Tops	Roots
	gm.	*gm.*
$CaH_4(PO_4)_2 \cdot H_2O$, in collodion bag	5.65	2.10
Rock Phosphate, in collodion bag	0.40	0.45
Rock Phosphate, saturated solution	4.90	1.85

with a saturated solution of rock phosphate. Cowpeas were again used as the test crops in the same nutrient solution as that used for the experiments already described. The saturated solution of rock phosphate was prepared by shaking 2 gm. of rock phosphate at frequent intervals for 5 days and then clarifying it by passing the solution through a Pasteur-Chamberlain filter. The concentration of phosphorus in the saturated solution of rock phosphate varied from 0.217 p.p.m. to 0.250 p.p.m., usually being closer to the latter figure. The solutions for the plants grown in the saturated solution of rock phosphate were changed twice daily in order to maintain the concentration of phosphorus as near its maximum as possible. The amounts of dry matter produced in 4 weeks from the different treatments are given in table 8.

The results show that when the phosphorus in solution from rock phosphate is maintained near its maximum concentration, the plants will make satisfactory growth. The plants in this case made almost as good growth as from the monocalcium phosphate. On the other hand, when the phosphorus had to dialyze from rock phosphate the growth was very unsatisfactory and amounted to only a small percentage of that made from monocalcium phosphate. Since

it has been shown previously (3) that cowpeas cannot utilize rock phosphate when applied in the solid form to quartz cultures, the evidence seems conclusive that the availability of rock phosphate is definitely associated with its rate of solution. The technique used did not permit testing the various theories which have been advanced governing the solubility of rock phosphate.

It was pointed out in the first experiments that the high phosphorus content of the roots may be associated with their fluorine content and that the presence of fluorine may be a factor in the availability of phosphorus to plants. Jacob[4]

TABLE 9 [5]

Analysis of fluorine-bearing materials

MATERIAL	FLUORINE	P_2O_5	
		Total	Citrate-insoluble
	per cent	*per cent*	*per cent*
(a) Calcium fluoride, synthetic	48.30	.....	.....
(b) Calcium fluoride, natural	46.20	.....	.....
(c) Sodium fluoride, 99.1 per cent NaF	44.80	.....	.....
(c) Sodium fluosilicate, 99.7 per cent Na_2SiF_6	60.40	.....	.....
(c) (d) Sodium aluminum fluoride, synthetic, 94.3 per cent Na_3AlF_6	51.20	.....	.....
(c) (d) Barium fluosilicate, 76.1 per cent $BaSiF_6$, 2.8 per cent BaF_2, remainder principally silica	31.60	.....	.....
(e) Fluorspar basic slag, No. B-11	1.29	11.06	9.21
(e) Curacao phosphate rock, No. 943	0.41	39.99	33.87
(e) Curacao phosphate rock, No. 985	0.70	38.22	33.80
(e) Christmas Island phosphate rock, No. 452	1.32	39.27	34.80
(e) Nauru Island phosphate rock, No. 1160	2.10	38.66	33.97
(e) Ocean Island phosphate rock, No. 451	2.97	40.15	37.51
(e) Tennessee brown-rock phosphate, No. B-14	3.79	33.86	31.19

(a) Made by double decomposition between calcium chloride and sodium fluoride.
(b) Fluorspar, Bureau of Standards sample 79.
(c) Sample supplied by the Insecticide Division, Bureau of Chemistry and Soils.
(d) Commercial insecticide material.
(e) Ground to 100 mesh.

has shown a definite relationship between the fluorine content of some phosphate rocks and the availability of the phosphorus as measured by chemical methods.

In order to test the effect of fluorine on the solubility of phosphorus in soils, varying amounts of fluorides and phosphates containing different percentages of fluorine were added to jars, each containing 10 kilos of Clarksville silt loam. The composition of the fluorine compounds[5] is given in table 9.

[4] Jacob, K. D. 1934 Private communication. Bur. Chem. and Soils, U. S. Dept. Agr., Washington, D. C.

[5] The writer is indebted to K. D. Jacob, Bureau of Chemistry and Soils, for the samples and analyses of the materials given in table 9.

The amounts of fluorine added were varied from 1 to 10 p.p.m. in order to simulate the fluorine content of the phosphates used. The phosphorus was

TABLE 10

Yields of Sudan grass grown in Clarksville silt loam with the variation in fluorine and phosphorus treatment indicated

SOURCE OF PHOSPHORUS	SOURCE OF FLUORINE	CONCENTRATION OF F IN THE SOIL	AVERAGE YIELD OVEN-DRY MATTER		
			First cutting	Second cutting	Total
		p.p.m.	*gm.*	*gm.*	*gm.*
None*	None	....	2.00	5.35	7.35
None	None	....	2.25	9.70	11.95
None	CaF_2	1.0	2.35	8.85	11.20
None	CaF_2	3.0	2.30	8.65	10.95
None	CaF_2	5.0	1.75	8.10	9.85
None	CaF_2	10.0	2.45	9.10	11.55
None	NaF	1.0	2.00	8.35	10.35
None	NaF	3.0	1.85	8.35	10.20
None	NaF	5.0	2.10	9.50	11.60
None	NaF	10.0	2.40	8.95	11.35
None	$BaSiF_6$	1.5	1.90	7.30	9.20
None	$BaSiF_6$	3.0	2.70	8.80	11.50
None	Na_3AlF_6	3.0	2.40	8.15	10.55
None	Na_2SiF_6	3.0	2.45	7.60	10.05
Fluorspar basic slag	Fluorspar basic slag	3.5	6.40	16.05	22.45
Phosphate rock 943	Phosphate rock	0.3	21.70	23.35	45.05
Phosphate rock 985	Phosphate rock	0.5	19.65	20.35	40.00
Phosphate rock 452	Phosphate rock	1.0	16.25	19.15	35.40
Phosphate rock 1160	Phosphate rock	1.6	14.70	23.60	38.30
Phosphate rock 451	Phosphate rock	2.2	8.15	23.50	31.55
Tenn. phosphate rock, B14	Phosphate rock	3.4	10.00	20.60	30.60
$CaH_4(PO_4)_2 \cdot H_2O$	None	0	23.30	21.25	44.55
$CaH_4(PO_4)_2 \cdot H_2O$	CaF_2	1.0	25.60	21.65	47.25
$CaH_4(PO_4)_2 \cdot H_2O$	CaF_2	3.0	22.35	21.80	44.15
$CaH_4(PO_4)_2 \cdot H_2O$	CaF_2	5.0	24.60	22.10	46.70
$CaH_4(PO_4)_2 \cdot H_2O$	CaF_2	10.0	25.35	21.95	47.30
$Ca_3(PO_4)_2$	None	0	21.55	20.30	41.85
$Ca_3(PO_4)_2$	CaF_2	1.0	23.25	21.00	44.25
$Ca_3(PO_4)_2$	CaF_2	3.0	23.10	21.70	44.80
$Ca_3(PO_4)_2$	CaF_2	5.0	23.20	20.55	43.75
$Ca_3(PO_4)_2$	CaF_2	10.0	22.25	22.10	44.35
$Ca_3(PO_4)_2$	NaF	1.0	21.20	19.80	41.00
$Ca_3(PO_4)_2$	NaF	3.0	20.95	23.05	44.00
$Ca_3(PO_4)_2$	NaF	5.0	21.65	24.30	45.95
$Ca_3(PO_4)_2$	NaF	10.0	21.55	22.20	43.75
$CaH_4(PO_4)_2 \cdot H_2O$	NaF	10.0	26.00	23.70	49.70

* No nitrogen or potassium added.

added at rates equivalent to 0.3 gm. P_2O_5 per jar, and ammonium sulfate and potassium chloride were added at the rate of 300 pounds per acre. Sudan

grass was seeded February 27, 1933, and cuttings were harvested on May 2 and June 5, 1933. The treatments and yields of Sudan grass are given in table 10. All jars except the first treatment received nitrogen and potassium fertilizers. The stubble was top-dressed with an equivalent of 300 pounds per acre each of ammonium sulfate and potassium chloride after the cutting made May 2. In the first cutting, differences were apparent in the size of plants growing in soil fertilized with the phosphate rocks containing fluorine. The largest plants were growing in the soil containing the rock with the smallest amount of fluorine. From this there was a gradual decrease in size of the plants as the percentage of fluorine in the phosphate rock increased. The differences were not so pronounced in the second cutting. There were no apparent undesirable effects where soluble fluorine salts were added to the soil.

The results show definitely that the addition to soils of fluorine compounds alone up to 10 p.p.m. of fluorine had no injurious effects on plant growth. Slight differences in the production of dry matter with some treatments can be attributed to plant variation, but in most instances larger concentrations of the same compound did not produce any injury.

The addition of fluorides with mono- and tribasic calcium phosphates did not depress the growth of the plants. CaF_2 was used as the standard fluorine treatment because it is present in rock phosphate or may result from the decomposition of rock phosphate. The other treatments are supplementary. If anything, there seemed to be a light stimulation in some treatments in the production of dry matter where the fluorides were added. Tri-calcium phosphate produced almost as much, or as much, dry matter as monocalcium phosphate when fluorides were also added to the soil.

The presence of chemically combined fluorine in phosphate rocks greatly affected the availability of the phosphorus to the plants. The availability of the phosphate decreased as the fluorine content of the rock increased. The effect is more apparent in the first crop. As a result of some readjustment in the soil or of the plant's becoming adjusted to different environmental conditions, these compounds are more efficient in producing dry matter in the second crop.

There is a definite relation between the fluorine content of the different phosphate rocks and of basic slag and the total amount of dry matter produced. The correlation factor between the milligrams of fluorine contained in the phosphate added to the soil and the total weight of dry matter produced was $-.895$. The odds are 99 to 1 that as the fluorine content of the rock phosphate increased the amount of dry matter decreased. In the studies made, the evidence is conclusive that the efficiency of the phosphorus in producing growth of plants was associated with the fluorine content of the rock phosphate. Moreover, a correlation factor of .7967 between the percentage of citrate-soluble phosphorus and the percentage of fluorine (table 9) shows significant odds, 19 to 1, that the availability as measured by chemical means is associated with the fluorine content of the rock.

The results of analyses made as previously described to determine the percentage of phosphorus in the plants are given in table 11.

Analyses were made on all the plants from these treatments but because the results of each group of treatments are similar only the results from the plants fertilized with phosphate rocks containing varying amounts of fluorine are included. It is to be regretted that it was not possible to separate the roots from the soil without losing many of the fine rootlets. Consequently no analyses were made to determine the fluorine content of the roots or tops. This would have given an opportunity to study further the possibility of fluorine's being precipitated in the roots.

The results from precipitated tricalcium phosphate as a source of phosphorus adds further to the information showing that this compound is a good source of phosphorus for crops in acid soils.

TABLE 11

Phosphorus content of Sudan grass grown in Clarksville silt loam with phosphates indicated

SOURCE OF PHOSPHORUS	AVERAGE PHOSPHORUS CONTENT				
	First cutting	Second cutting	First cutting	Second cutting	Total
	per cent	*per cent*	*mgm.*	*mgm.*	*mgm.*
None added	0.142	0.087	3.20	8.40	11.60
Fluorspar basic slag	0.142	0.090	9.05	14.35	23.40
Phosphate rock 943	0.125	0.087	26.90	20.35	47.25
Phosphate rock 985	0.140	0.098	27.40	19.90	47.30
Phosphate rock 452	0.130	0.095	21.05	18.10	39.15
Phosphate rock 1160	0.125	0.110	18.35	25.70	44.05
Phosphate rock 451	0.137	0.101	11.00	23.55	34.55
Phosphate rock, Tenn	0.128	0.101	12.80	20.70	33.50
$CaH_4(PO_4)_2 \cdot H_2O$	0.126	0.103	29.10	22.00	51.10
$Ca_3(PO_4)_2$	0.117	0.103	25.20	20.90	46.10

The results show that, as the amount of fluorine added in the fertilizer increases, the amount of phosphorus taken up by the plant decreases. A correlation factor of $-.9075$ gives odds greater than 99 to 1 that the relationship is not due to chance occurrence and shows that this relationship is specific for the phosphate rocks studied.

The results show very conclusively that the total amounts of dry matter produced and the total amounts of phosphorus absorbed from the phosphate rocks were intimately associated with their fluorine content. This would seem to be nothing more than a direct result of the solubility of the phosphorus in the phosphate rock. However, when the correlation is calculated separately for the first and second cuttings it is found that only in the first cutting is there a highly significant correlation between the fluorine content of the phosphate rocks and the yields of dry matter and the amounts of phosphorus absorbed. Moreover, the results from the second cutting not only show no correlation

between the production of dry matter and phosphorus absorbed with the fluorine added but in five out of seven treatments with phosphate rocks at least as much dry matter was produced as from monocalcium phosphate. In addition the amounts of phosphorus absorbed by the plants were in two cases larger than, in two about the same as, in two slightly less than, and in one considerably less than from monocalcium phosphate. However, in five out of seven treatments, the amount of phosphorus absorbed was as great as, or greater than, within limits of error, that absorbed from tricalcium phosphate. Moreover, more phosphorus was absorbed in the second cutting than in the first from those soils fertilized with samples 1160, 451, and Tennessee, whereas with monocalcium and all other phosphates, appreciably less phosphorus was absorbed by the plants of the second cutting.

The increased absorption can be explained in part as the result of increased root development, giving the plant a larger feeding area. This, however, does not explain the fact that the increases in phosphorus absorbed by the second cutting occurred where the phosphate rocks contained the larger percentages of fluorine and the smaller percentages of their phosphorus in a citrate-insoluble form. Since the production of dry matter and the absorption of phosphorus in this experiment were specifically associated with the fluorine content of the phosphate rocks it seems that some factor other than increased root development is responsible for the differences noted in the uptake of phosphorus in the second cutting. It is hoped that future experiments will aid in the solution of this problem.

SUMMARY

Experiments were conducted to study the effect of soluble fluorine compounds on the germination of seeds and the growth of plants. The influence of fluorine on the availability of phosphorus to plants was also studied.

Concentrations of fluorine as large as 50 p.p.m. did not seem to decrease significantly the germination of Sudan grass, cowpea, soybean, red clover, or white Dutch clover seeds. In fact, the germination of white Dutch clover was greatly enhanced by the presence of calcium fluoride and sodium fluosilicate.

The addition of soluble fluorides up to 10 p.p.m. fluorine did not materially decrease the amounts of dry matter produced by cowpeas grown in culture solution. The variations noted were attributed to variations in the plants.

Fluorine in the plants was found largely in the roots. Only when the amounts of fluorine in the roots were relatively large was fluorine present in the tops.

A general trend for the percentage phosphorus in the tops to decrease as the percentage of fluorine in the roots increased was noted and an explanation suggested.

The addition of soluble fluorine compounds to the soil did not seem to affect the availability of the phosphorus in the soil or that added as monocalcium phosphate.

The presence of fluorine in naturally occurring phosphate rocks greatly influenced the availability of their phosphorus to plants. A specific correlation was found between the total amounts of dry matter produced by Sudan grass grown in an acid silt loam soil and the milligrams of fluorine added to the soil in the phosphate rocks studied. There was also a specific correlation between the milligrams of phosphorus found in the plants and the milligrams of fluorine added to the soil in the phosphate rocks.

Evidence is given to substantiate the theory that the availability of the phosphorus in rock phosphate is largely a matter of the rate of solution of the rock phosphate. It is also suggested that the availability to plants of the phosphorus in phosphate rock is associated with the percentage of fluorine in the phosphate rock.

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THE EFFECT OF NITROGEN CONTENT OF RYE ON ITS RATE OF DECOMPOSITION

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The rate of decomposition of organic matter in soils under aerobic conditions is greatly influenced by its nitrogen content. Investigations concerning the effect of percentage nitrogen of organic matter on the rate of decomposition with which the writer is acquainted have been made using materials of different kind or of the same kind but of different age.

In an experiment in the greenhouse involving the growth of rye with and without Austrian winter peas with the addition of varying amounts of nitrate of soda, rye was obtained which varied in nitrogen content from 0.64 per cent to 1.83 per cent. The availability of this material afforded an opportunity to determine the effect of the nitrogen content of rye on its rate of decomposition in the soil as measured by the rate of evolution of CO_2. This study, therefore, involved a comparison of plant materials of the same kind and age, but not necessarily at the same stage of maturity.

The soil used was a mixture of 10 per cent Houston clay and 90 per cent Oktibbeha fine sandy loam. The Oktibbeha fine sandy loam was very unproductive, whereas the Houston clay was fertile and very high in available phosphorus. The Houston clay was added to supply a good flora and available phosphorus. Two grams of air-dried rye was mixed with 201 gm. of air-dried soil containing 0.55 per cent water, and 30 cc. of water was added. The soil was then crumbled to distribute the water evenly throughout the sample. The water content was comparable to that of a field soil that contains the requisite amount of water to plow well and leave the soil in good tilth.

Then the soil was put into 1,000-cc. Erlenmeyer flasks. The flasks were closed with a 2-hole rubber stopper carrying a long glass tube extending to the bottom of the flask and a short glass tube extending just through the stopper. Glass wool was put over the end of the short tube inside the flask to keep the soil out of it. The flasks were made air-tight by putting over the outer ends of the tubes rubber tubes closed at one end with pointed glass stoppers. Then the flasks with their contents were inverted in their support and maintained at room temperature. The experiment was started on April 5, 1933, and the carbon dioxide was determined on the dates indicated in table 1. When the CO_2 determinations were made, the flasks were connected in a gas train. The members of the train in order were: soda lime column, soil flask, H_2SO_4 tube,

TABLE 1

Effect of the nitrogen content on the rate of decomposition of rye as measured by carbon dioxide evolution

NITROGEN IN RYE†	MILLIGRAMS OF CO_2 EVOLVED PER 24 HOURS FROM THE RYE											TOTAL
	April 5–7	April 7–8	April 8–9	April 9–11	April 11–14	April 14–18	April 18–25	April 25–May 8	May 8–June 1	June 1–June 28	June 28–Aug. 2	April 5–Aug. 2
per cent												
0.64	126	85	62	42	28.0	15.8	13.7	9.3	6.46	4.56	2.51	1216
0.83	138	98	71	48	29.3	16.5	14.9	10.9	7.67	5.37	2.31	1351
0.83	130	112	70	47	28.7	17.0	14.1	8.5	6.08	4.33	2.09	1236
1.03	162	125	85	57	34.0	18.8	15.6	10.2	6.92	4.22	1.57	1400
1.04	161	124	84	56	35.0	19.3	16.1	10.1	7.29	4.26	1.20	1400
1.11	154	129	87	57	34.3	18.8	16.3	10.4	7.67	4.11	0.91	1394
1.26	170	144	97	63	37.3	21.3	17.0	11.5	6.67	2.63	1.03	1438
1.26	178	165	103	66	37.3	18.8	15.7	8.9	4.58	1.70	0.40	1341
1.31	182	175	111	69	41.0	21.8	17.6	10.8	6.54	2.78	0.80	1522
1.41	165	169	105	67	42.0	22.5	18.1	11.5	3.71	2.30	1.09	1421
1.50	180	188	111	71	41.7	22.8	18.4	10.5	5.13	2.63	0.80	1506
1.83	185	238	135	80	42.0	23.8	17.7	7.3	4.17	2.11	0.51	1519
Check.....	14.5	9.50	8.80	5.85	5.13	3.45	2.69	2.26	2.33	2.23	1.69	312
Correlation coefficient	.890± .0627*	.978± .0130	.983± .0103	.983± .0099	.927± .0422	.943± .0332	.880± .0681	−.205± .2888	−.667± .1673	−.826± .0956	−.853± .0823	

* Standard error.

† The nitrogen determinations were done by Marvin Gieger, experiment station chemist.

$CaCl_2$ tube, ascarite tube, $CaCl_2$ tube, and a 3,600-cc. water bottle from which the water was siphoned in order to draw air through the train. The soil flasks were so connected that the air entered them through the long tube and passed downward, finally passing through the soil and out through the short tube, thus facilitating the removal of the carbon dioxide. The carbon dioxide was swept out of the soil flask by drawing 3600 cc. of CO_2-free air through the train. The CO_2 was absorbed by the ascarite and determined by weighing the tube before and after the absorption.

The data are reported in table 1. The soil microörganisms require nitrogen as well as other nutrients, and the quantity of nitrogen consumed by the soil microörganisms in the decomposition of the rye is very probably directly proportional to the quantities of rye decomposed as measured by the carbon dioxide evolved. The correlation coefficients obtained during the first month of the test are positive and nearly 1, which indicates almost perfect correlation between the percentage of nitrogen in rye and the rate of decomposition of rye. After one month the correlation coefficients become negative and at the last determination during the fourth month the coefficient of correlation was $-.853 \pm .0823$ (standard error) which means that the decomposition of rye at that stage is inversely proportional to its nitrogen content. Soil microorganisms draw upon the soil for nitrogen to build their bodies when the organic material being decomposed is low in nitrogen. The rye with a higher nitrogen content will require less soil nitrogen in the early stages of decomposition because that liberated by the decomposed rye will be used, and more nitrogen will be liberated by the rye of high nitrogen content. In the later stages of the experiment the rye of low nitrogen content was decomposing at a more rapid rate, which indicates that larger quantities of nitrogen would be tied up in the microörganisms.

SOME CHEMICAL AND BIOLOGICAL CHANGES PRODUCED IN A FOX SANDY LOAM BY CERTAIN SOIL MANAGEMENT PRACTICES[1]

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The effects of cropping systems and fertilizer and lime applications on soils under experimental conditions have been measured chiefly in terms of differences in plant yields. In some cases changes in the organic matter content of the soil have been measured, and frequently the quantities of available plant nutrients in the soil of treated and untreated plats have been determined. Changes in the biological conditions in soils, however, such as nitrifying power, numbers of bacteria and fungi, and carbon dioxide production, resulting from soil treatments have been studied to a less extent.

In 1917, the Soils Section of Michigan Experiment Station placed under experimental treatment a field of Fox sandy loam soil which had fallen to such a low state of fertility that it had been uncropped for several years. During the succeeding years many of the treated plats attained a fairly high state of fertility as measured by crop yields, as much as 50 bushels of wheat to the acre having been grown on some plats. Marked differences occurred, however, in the crop yields obtained from plats receiving different treatments.

This investigation was carried on to determine to what extent certain chemical and biological changes had taken place in the soil of the plats receiving different treatments, and to find what correlation might exist among the various data collected.

REVIEW OF LITERATURE

Literature dealing with the relationships of chemical and biological activities in soil and the crop producing power of the soil has been thoroughly reviewed elsewhere (9, 10), and hence no review of the literature is included in this paper.

EXPERIMENTAL

Record of soil treatment and cropping history of plats selected for the investigation

For the purposes of this investigation eight plats were selected from the experimental field.

[1] A thesis presented to the faculty of the Michigan State College in partial fulfillment of the requirements for the degree of doctor of philosophy. Published, with the approval of the Director, as Journal Article No. 190 n.s. of the Michigan Agricultural Experiment Station.

[2] The writer expresses his sincere appreciation to Dr. C. E. Miller for assistance throughout the course of this investigation.

As the Fox sandy loam is a strongly acid soil, an application of 3 tons of ground limestone to the acre was made at the beginning of the field experiment to all except the check plats. Fertilizers were applied at the following rates per acre: potassium, 100 pounds 50 per cent KCl; nitrogen, 100 pounds $NaNO_3$; phosphorus, 200 pounds 16 per cent superphosphate; rock phosphate, 1,000 pounds; gypsum, 86 pounds. All of the fertilizers were applied before the crops were planted, with the exception of nitrogen for fall seeded grain. Of this, 40 per cent was applied in the fall, and 60 per cent in the spring until 1920, when the proportions were changed to 20 per cent in the fall and 80 per cent in the spring. Periodic applications of the fertilizers were made as shown in table 1, and according to the amounts already given.

The cropping history of these plats since they have been under experimentation is as follows: soybeans, 1917; rye, 1918; wheat, 1919; sweet clover, 1920,

TABLE 1

Periodic application of fertilizers to the designated plats

SOIL		YEAR OF APPLICATION										
Number	Field* treatment	1917	1918	1919	1922	1923	1924	1926	1927	1928	1929	1930
301N	None	.....	....	.....	.....	....	.....	....	....	.....	.....	....
301S	Lime	L	....	.....	.....	....	.....	....	....	.....	.....	....
302	LNPK	LNPK	N	PN	PNK	N	PNK	P	N	PNK	NP	N
305	LPK	LPK	....	P	PK	....	PK	P	....	PK	P	....
307	LN	LN	N	N	N	N	N	....	N	N	N	....
308	LK	LK	....	.....	K	....	K	....	.....	K	.....	....
309	LP	LP	....	P	P	....	P	P	....	P	P	....
310	LRP.C	LRP.C	....	.....	RP.C	....	.....	....	....	RP.C	.....	....

*L = Lime in the form of ground limestone; K = Potassium as potassium chloride; RP. = Phosphorus as rock phosphate; N = Nitrogen as sodium nitrate; P = Phosphorus as superphosphate; C = Calcium sulfate as gypsum. This legend applies throughout this paper.

1921; rye, 1922; corn, 1923; wheat, 1924; sweet clover, 1925; soybeans, 1926; wheat, 1927; corn, 1928; oats, 1929; and wheat, 1930, 1931. The soybean crop in 1926 was plowed under to supplement the organic matter derived from crop residues. The yield was determined before the crop was plowed under. Other crops were removed, no straw, stover, or similar material being added to the soil.

Method of taking soil samples

Soil samples of sufficient quantity for all the laboratory studies were taken from the plats in the fall of 1931.

For a representative compositive sample, five samples were taken at systematically located points on each plat and thoroughly mixed. Samples were taken by removing and discarding the surface inch of soil and then taking with

a spade the desired amount of plowed soil to a depth of 6 to 8 inches. After thorough mixing and screening to remove stones and large particles of undecomposed organic matter, aliquots were taken, air dried, and stored in sterilized containers.

Laboratory methods

Nitrogen was determined by the method given for soils in the Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists (1). Loss on ignition was determined as a rough measure of organic content, since the soils contained no carbonates. The reaction, in terms of pH, was determined on air-dry soil by the quinhydrone method as described by Bauer (2). Available phosphorus in pounds per acre was obtained by the method of Truog (5). Fred and Waksman's (3) reduction method was used

TABLE 2

Chemical analyses of soils and crop yields in pounds per acre and in per cent based on the results from the untreated soil, in relation to soil treatment

SOIL		REACTION	CROP YIELDS		AVAILABLE P_2O_5		TOTAL NITROGEN		IGNITION LOSS	
Number	Field treatment	pH	Pounds of dry matter	Per cent	Pounds per acre	Per cent	Pounds per acre	Per cent	Pounds per acre	Per cent
301N	No treatment	4.71	8,857	100	23	100	1380	100	34,200	100
301S	Lime	5.15	26,399	298	26	112	1300	94	35,600	104
302	LNPK	5.59	42,253	478	33	144	1420	103	41,200	120
305	LPK	5.45	37,425	423	34	148	1420	103	41,400	121
307	LN	5.67	32,738	370	29	126	1200	87	36,200	106
308	LK	5.74	29,288	331	30	131	1220	89	36,600	107
309	LP	5.61	25,692	290	32	139	1200	87	34,600	101
310	LRP.C	5.59	27,363	309	40	174	1120	81	34,000	100

to determine nitrate nitrogen. Numbers of bacteria and fungi were obtained by taking the average count from six agar plates of the respective media used. Nitrification and carbon dioxide production methods are described in the respective studies dealing with these substances.

RELATION BETWEEN SOIL TREATMENT, CROP PRODUCTION, SOIL REACTION, AND SOME AVAILABLE NUTRIENTS

Because of the influence of seasonal variations on crop production, which tend to modify differences due to fertilizer treatment and other factors affecting productivity, it was deemed advisable to express the yields of the different plats in terms of pounds of dry plant material produced during the entire period they have been under experimentation. Table 2 presents a comparison between crop yield and soil reaction, quantities of available phosphorus, loss on ignition, and nitrogen.

Although the supply of available phosphorus is low in all the soils, those receiving phosphate applications have the largest amounts. This is especially true of soils 310N and 309, which were treated with rock phosphate and superphosphate, respectively. Since the available supply of phosphorus is low, any difference due to soil treatment may be expected to have a marked influence on the chemical and biological conditions in these plats.

The soils receiving combinations of lime, nitrogen, and phosphorus were higher in nitrogen and loss on ignition than those receiving lime and single element treatment. Since all the soils were comparatively low in nitrogen and organic matter, additions of these substances should have some effect on the biological activities in these soils.

The data show that lime raised the pH over that of the untreated soil, but not so much as did lime and fertilizers together. Though the differences in reaction between soils receiving lime alone, no treatment, and lime plus fertilizer are appreciable it is doubtful if the differences in reaction between soils receiving different combinations of lime and fertilizers are large enough to have any appreciable effect on the biological and chemical relationships in the soil.

All of the field treatments have increased the yield of crops over those from the untreated soil. Lime alone has given a very marked increase, and lime with combinations of nitrogen, phosphorus, and potassium has given the greatest increases. Combinations of lime and either superphosphate or rock phosphate have shown the smallest increases in crop yields over the untreated soil, the crop yields being about the same as, or slightly greater than, those from lime alone.

NUMBERS OF BACTERIA AND FUNGI IN RELATION TO SOIL TREATMENT AND SOME AVAILABLE NUTRIENTS

If available nutrients and numbers of microörganisms in soils are related and are equally affected by soil treatment, as stated by Waksman (9), then a determination of the number of the more important groups of microörganisms and the quantities of available nutrients should show some definite relationships for these soils. The number of fungi developing on acid agar media and of bacteria developing on Brown's albuminate agar media from air-dry samples of the different soils were determined. The results given in table 3 and figure 1 show the actual numbers of organisms present and also the numbers as per cent based on the number found in the untreated soil. The curves are constructed from the percentage data.

Lime alone greatly increased the number of bacteria over the number found in the untreated soil, and lime in combination with fertilizing elements enhanced this increase. This increase in numbers was especially marked for those soils receiving phosphorus with lime or with lime and other fertilizing elements. The evidence points to the important part played by phosphorus in bacterial development in these soils.

All field treatments increased the number of fungi developing on agar plates over that from untreated soil. This increase was exceedingly great for soils 308 and 309, which received lime plus potassium and lime plus superphosphate, respectively. Additions of lime alone, lime plus nitrogen, lime plus rock phosphate, and combinations of lime, phosphorus, and potassium gave only small increases in numbers of fungi in the soil. These results indicate no consistent relationship between soil treatment and number of fungi present.

TABLE 3

Numbers of bacteria and fungi in relation to soil treatment

SOILS		MICROÖRGANISMS			
		Bacteria		Fungi	
Number	Treatment	Number	Per cent	Number	Per cent
301N	None	567,000	100	347,000	100
301S	Lime	1,388,000	245	443,000	128
302	LNPK	1,659,000	293	624,000	180
305	LPK	2,028,000	358	444,000	128
307	LN	1,725,000	305	433,000	125
308	LK	1,614,000	285	905,000	261
309	LP	1,902,000	336	964,000	277
310N	LRP.C	1,917,000	338	438,000	126

TABLE 4

Rate of nitrification of urea and several ammonium salts by one of the soils studied

SOIL TREATMENT	NO_3 NITROGEN END OF 4TH WEEK	NO_3 BASED ON RESULT FOR CHECK
	mgm.	*per cent*
Check	3.28	100
$(NH_4)_2SO_4$	5.84	178
NH_4Cl	1.95	60
$(NH_4)_2HPO_4$	10.41	318
$(NH_4)_2C_2O_4$	11.28	344
$NH_4C_2H_3O_2$	10.11	308
$(NH_4)_3C_6H_5O_7$	10.48	320
$(NH_4)_2CO$	11.68	357

A comparison of bacterial numbers and available nutrients shows a distinct relationship between the supply of available phosphorus and numbers of bacteria, except in case of soil 310N. Loss on ignition correlates well with the number of bacteria, except for soils 309 and 310N. Total nitrogen content shows the same correlation with numbers of bacteria as does loss on ignition except in the case of soil 301N. Numbers of fungi showed little relation to soil treatment, soil reaction, or content of available phosphorus, total nitrogen, or loss on ignition.

NITRIFICATION OF NITROGENOUS MATERIALS IN SOILS AND ITS RELATION TO OTHER SOIL PROCESSES

Nitrification is considered by some investigators as a true measure of soil productivity, since the conditions most favorable for the nitrifying process are very similar to those for plant growth. If this be true or partly so, a study of nitrification in these soils should give some information of value in determining the changes taking place in soils due to soil treatment.

To determine the most suitable materials for nitrification studies in these soils, urea and a group of organic and inorganic salts of ammonium were selected for a preliminary trial on one of the soils used in this investigation. The materials were added in sufficient quantities to give 50 mgm. of nitrogen per 100 gm. of air-dried soil. No attempt was made to determine the most suitable quantity of nitrogen, because several investigators have shown that 30 to 50 mgm. of nitrogen per 100 gm. of soil is well suited for nitrification studies. A sufficient number of soil samples were prepared to permit of determining nitrate production at weekly intervals. The data given in table 4 show only the nitrates found at the end of the 4-week period.

More nitrates were produced from urea and all the salts except ammonium chloride, than from the soil's own supply of nitrogen. Ammonium sulfate was also a poor source of nitrifiable nitrogen. This decrease in nitrification with the addition of ammonium chloride and the relatively slow nitrification of ammonium sulfate is in agreement with the results of Kulik (4) and Turchin (7). Urea was the most rapidly nitrified of the materials used, followed closely by the organic salts of ammonium. Diammonium phosphate was not nitrified rapidly during the first week, but at the end of 20 days it was well nitrified.

For the next study, urea and diammonium phosphate were selected, because the former consistently produced the greatest amounts of nitrates and because the latter produced sufficient quantities of nitrates for the purposes of the study and in addition the phosphate factor was eliminated for all plot treatments. To these were added ground alfalfa and cottonseed meal in order to have a greater variety of materials, since it is maintained (8) that a better picture of nitrification in soils can be obtained by using several materials and more than one method of procedure. The materials were added to 100 gm. of air-dried soil in quantities to give 50 mgm. of nitrogen for urea and diammonium phosphate and 0.5 per cent of the organic plant materials. The usual soil tumbler method was followed throughout the study of nitrification.

Nitrate production from the four applied materials, in milligrams and in per cent based on results for the untreated soil, are given in table 5. Loss on ignition, available phosphorus, and total nitrogen content of the soils on a percentage basis are also included. It is evident from the data that field treatment has changed the ability of these soils to nitrify certain nitrogenous materials. The combination of lime, phosphorus, and potassium in soil 305 has resulted in the greatest nitrification power, followed closely by lime, phos-

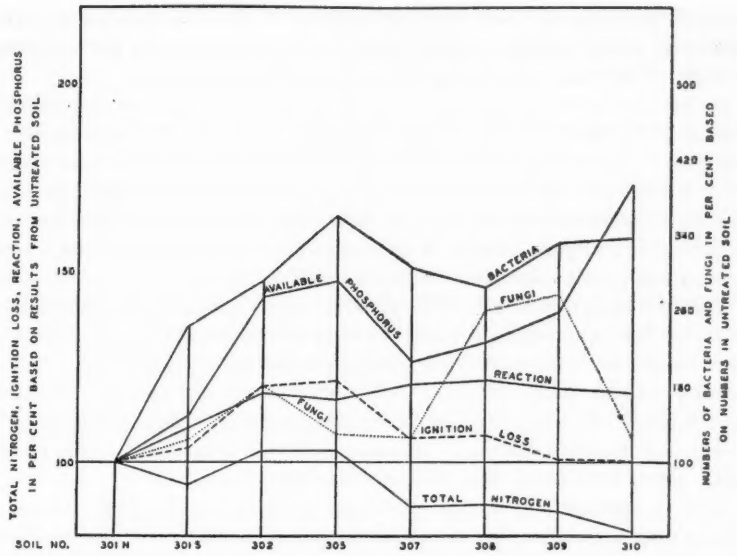

FIG. 1. NUMBERS OF BACTERIA AND FUNGI IN RELATION TO SOIL TREATMENT, SOIL REACTION, CONTENT OF TOTAL NITROGEN, AVAILABLE PHOSPHORUS, AND IGNITION LOSS

TABLE 5

Nitrate production from different materials in relation to field treatment of soils and to loss on ignition, total nitrogen, and available phosphorus content

SOIL		NITRATE NITROGEN AT END OF 28-DAY PERIOD IN MGM. PER 100 GM. OF SOIL AND IN PER CENT BASED ON RESULT FOR UNTREATED SOIL									LOSS ON IGNITION, AVAILABLE P, AND TOTAL N IN PER CENT BASED ON RESULT FOR UNTREATED SOIL		
Number	Field treatment	Alfalfa		Cotton seed meal		$(NH_4)_2HPO_4$		$(NH_2)_2CO$		Average for all treatments	Available P	Loss on ignition	Total N
		mgm.	*per cent*	*mgm.*	*per cent*	*mgm.*	*per cent*	*mgm.*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
301N	None	3.27	100	5.35	100	2.55	100	8.40	100	100	100	100	100
301S	Lime	4.43	135	8.45	158	4.43	173	10.35	123	147	112	104	94
302	LNPK	5.40	165	10.40	195	6.60	259	12.98	155	194	144	120	103
305	LPK	6.00	183	12.50	234	7.28	285	14.43	172	218	148	121	103
307	LN	5.04	155	10.20	191	6.88	270	11.25	134	187	126	106	87
308	LK	4.92	150	11.40	213	6.53	256	11.75	140	189	131	107	89
309	LP	4.80	147	11.30	211	6.90	270	11.59	138	191	139	101	87
310	LRP.C	3.65	112	9.10	170	5.35	238	9.28	111	180	174	100	81

phorus, nitrogen, and potassium in soil 302. Lime plus superphosphate, lime plus potassium, and lime plus nitrogen produced, in the order given, greater quantities of nitrates than lime plus rock phosphate or lime alone. Of impor-

tance is the relatively low nitrifying capacity of the soil receiving no field treatment, which indicates a raising of the nitrifying capacity, for the materials studied, of the other soils through lime and fertilizer treatment.

A close correlation is observed for nitrification of urea and cottonseed meal and for alfalfa meal and diammonium phosphate. The first two materials were nitrified to a greater extent during this period than the latter two. Although there is a difference in rate at which any soil nitrifies these materials, the relationship between soil treatment and nitrification of all of them is similar enough to permit of taking an average of the results for the four materials on a percentage basis for a comparison with other soil factors.

With the exception of soil 310N, which is high in available phosphorus and relatively low in nitrifying capacity for urea and cottonseed meal, there is a close correlation between available phosphorus and nitrate production. Nitrification of alfalfa meal correlates closely with available phosphorus, except for soils 309 and 310, which are high in this element and relatively low in nitrate production from this material. Nitrate production from diammonium phosphate shows little correlation with available phosphorus.

Loss on ignition and nitrate production from cottonseed meal and urea show a clear correlation, but nitrate production from alfalfa and diammonium phosphate shows less relationship.

Total nitrogen shows a similar relation to nitrate production from the different materials, as does loss on ignition.

CARBON DIOXIDE PRODUCTION FROM CELLULOSE IN RELATION TO SOIL TREATMENT

It has been claimed by some investigators that a measure of carbon dioxide production furnishes a better index of biological activity in soils than any other method yet devised. A measure of carbon dioxide production from decomposable material in the soils under study should indicate, therefore, changes related to soil treatment, if changes of measurable magnitude have taken place. Cellulose was used as the source of energy. It has further been shown that certain elements, namely nitrogen and phosphorus, influence the rate of CO_2 production from cellulose, and, since these soils are all low in these elements but show differences due to fertilizer treatment, it was deemed advisable to make some determinations in which phosphorus or nitrogen was added with cellulose to the soils. For additional comparisons, potassium and calcium in the form of chlorides were added with cellulose to some cultures. "Ascarite" was used for absorbing the carbon dioxide. The method used is similar to the one found entirely satisfactory for this kind of a study by Turk (6).

Results of carbon dioxide production determinations in milligrams per 100 gm. of soil and in per cent based on results from the untreated soil are give in table 6. A comparison of the milligrams of carbon dioxide produced under the different treatments shows that nitrate nitrogen was most effective in hastening the decomposition of cellulose. These results substantiate conclusions cited in the literature that nitrogen plays a very important part in

cellulose decomposition as measured by CO_2 production. It bears out the statement made in an earlier part of this paper that these soils being extremely low in total nitrogen would be expected to respond to applications of this element.

Additions of available phosphorus increased the production of carbon dioxide from cellulose much more than did additions of calcium or potassium chloride. This stimulation of carbon dioxide production from cellulose by phosphorus additions follows from the fact that these soils are relatively low in this element and that available phosphorus supply has been shown to influence the rate of cellulose decomposition as measured by CO_2 production.

Additions of calcium and potassium chlorides increased to a limited extent the production of carbon dioxide from cellulose over that from the soils receiv-

TABLE 6

Carbon dioxide production from cellulose with different chemicals added in relation to soil treatment

SOIL		CARBON DIOXIDE PRODUCTION IN 24 DAYS										
Number	Field treatment	Cellulose		$CaCl_2$ + cellulose		KCl + cellulose		Na_2HPO_4 + cellulose		$NaNO_3$ + cellulose		Average for all treatments
		mgm.	*per cent*	*mgm.*	*per cent*	*mgm.*	*per cent*	*mgm.*	*per cent*	*mgm.*	*per cent*	*per cent*
301N	None	149	100	126	100	130	100	294	100	493	100	100
301S	Lime	169	113	151	120	166	127	231	78	548	111	110
302	LNPK	204	137	213	169	216	166	268	91	619	126	138
305	LPK	223	150	231	183	248	191	286	98	643	130	150
307	LN	171	115	216	171	238	183	263	89	614	124	136
308	LK	171	115	207	164	224	172	250	85	629	127	132
309	LP	158	106	190	151	197	152	243	83	560	114	121
310	LRP.C	122	82	181	144	174	134	214	73	585	118	111

ing cellulose alone. Potassium chloride seemed to be more effective in this respect than calcium chloride.

When the results of carbon dioxide production from cellulose with certain chemicals added is calculated in per cent based on results for the untreated soil, as shown in table 6, the effect of soil treatment on this process may be demonstrated. The results show a marked increase in the soil's ability to produce CO_2 from cellulose for all fertilizer treatments as compared to the untreated soil. Lime alone increased the production of CO_2 from cellulose over the untreated soil, but not to the extent that combinations of lime, nitrogen, phosphorus, and potassium did.

The production of CO_2 from cellulose was greatest in soil 305, which had received lime, potassium, and phosphorus in the field. Soil 302 followed 305 in CO_2 production from cellulose alone, but combinations of lime plus nitrogen, lime plus potassium, and lime plus phosphorus were little if any better than lime alone in increasing the production of CO_2 from cellulose in these soils.

The relation between carbon dioxide production from cellulose alone, total nitrogen, and available phosphorus in the soil further emphasizes the importance of these elements, especially nitrogen, in this process. Carbon dioxide production from cellulose with potassium and calcium chlorides added show a close relation to total soil nitrogen for all soils.

INTERRELATIONS BETWEEN NITRIFICATION, CARBON DIOXIDE PRODUCTION, BACTERIAL NUMBERS, CROP YIELDS, AND AVAILABLE NUTRIENTS

The previous studies showed that fertilizer treatments produced some chemical and biological differences in the soil under study. It is of interest at

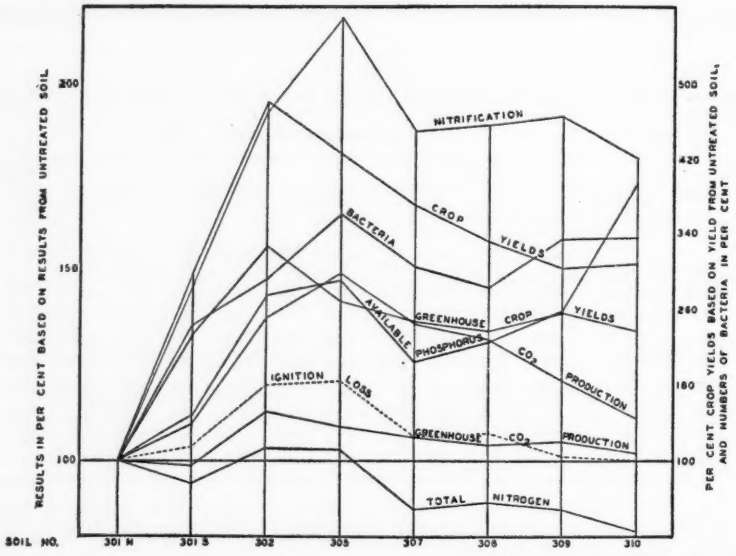

FIG. 2. INTERRELATION BETWEEN NITRATE PRODUCTION, CONTENT OF AVAILABLE PHOSPHORUS, TOTAL NITROGEN, AND IGNITION LOSS, BACTERIAL NUMBERS, CROP YIELDS IN THE FIELD AND GREENHOUSE, AND CARBON DIOXIDE PRODUCTION FROM FIELD AND GREENHOUSE SAMPLES IN SOILS RECEIVING DIFFERENT FIELD TREATMENTS

this time to make a comparison of all the relationships, in order to obtain a better picture of conditions as a whole in these soils. In figure 2 all of the results are presented, expressed in per cent, the data from soil 301N, which received no fertilizer treatment, being used as a basis. For convenience, results from greenhouse studies presented on following pages are included in the figure. These will be discussed later.

Soil 305, treated in the field with lime, phosphorus, and potassium, showed the greatest nitrifying power, carbon dioxide production, number of bacteria, and loss on ignition and ranked second in the production of crops. Soil 302,

treated in the field with lime, nitrogen, phosphorus, and potassium, produced the largest yields of crops but ranked second to soil 305 in loss on ignition, nitrifying capacity, and carbon dioxide production and equalled it in total nitrogen content. The soil treatments in their order of efficiency for maintaining organic content of the soil, as indicated by loss on ignition, were: LPK, LNPK, LK, LN, L, LP, with LRPC and no treatment on a par.

Available phosphorus was proportionately higher in those soils receiving this element in the field than in those receiving lime or combinations of lime and other fertilizing elements. This condition was especially pronounced in soil 310, which received large amounts of rock phosphate. From these results it is evident that the supply of available phosphorus can be increased in these soils by additions of certain forms of this element; especially is this true where large amounts are applied and relatively small amounts are removed by the crops.

Field treatments consisting of lime plus superphosphate and of lime plus rock phosphate and gyspum affected all factors studied, except available phosphorus and bacterial numbers, to a less extent than did any treatment aside from lime alone.

The results as a whole indicate that treatments including combinations of fertilizer elements and lime had a greater effect on all factors studied than did application of the elements singly with lime. Furthermore, in combination with lime no single element was more effective in all respects than were other elements. These data clearly indicate that the soil studied is in need of all three fertilizing elements. The need for potassium and phosphorus is evidently greater than for nitrogen, since the effect of the LPK treatment is equal to or greater than the effect of the LNPK in all respects except crop yield.

GREENHOUSE STUDIES

To determine further the effect of soil treatment on chemical composition and biological processes in the soil, crops of sweet clover, rye, and soybeans were grown on the soils in pot cultures in the greenhouse. The crops were cut after a 12-week growth period and air dried, and weights were determined. For carbon dioxide production study, the harvested material was then ground and returned to a portion of the soil on which it had grown. It was the object of this study to determine whether soil differences found in the previous work on these soils could be measured by crop yields in the greenhouse and whether carbon dioxide production, when the crops grown were returned to the soils, was comparable to results from previous carbon dioxide production studies.

Duplicate 2-gallon pots of the different soils were used. The moisture content was maintained by weighing the pots at frequent intervals and bringing up to weight with distilled water. The crop yields in grams and in per cent based on the yield from the untreated soil are given in table 7.

The results show that soil 302, treated in the field with lime, nitrogen, phosphorus, and potassium, produced the largest yields of all three crops and

that soil 305, treated in the field with lime, potassium, and phosphorus ranked second in yield of plant materials. These results are in accord with those obtained under field conditions. Field treatments of lime plus nitrogen, and of lime plus potassium, gave approximately the same yields of leguminous plant material as did lime alone, but the yields were not so large as for soils 302, 305, and those receiving lime with phosphorus. The soil receiving lime alone gave larger yields of all crops in the greenhouse than did the untreated soil, but not so large as soils receiving any combination of fertilizer with lime.

The unusually low yields of all crops on the untreated soil 301N is of special interest as they indicate the low fertility of the soil where no fertilizer treatments have been made. This decrease in ability to produce crops is especially marked for the legumes, where considerable difficulty was experienced in obtaining measurable yields of plant material. Undoubtedly this condition was due primarily to a deficiency of lime.

TABLE 7

Crop yields from greenhouse pot studies expressed as grams of air-dry plant tissue and in per cent based on results from untreated soil

SOIL		SWEET CLOVER		RYE		SOYBEANS		AVERAGE
Number	Field treatment							
		gm.	*per cent*	*gm.*	*per cent*	*gm.*	*per cent*	*per cent*
301N	None	1.00	100	15.15	100	6.14	100	100
301S	Lime	4.36	436	16.45	108	9.55	155	233
302	LNPK	6.61	661	22.35	148	10.74	175	328
305	LPK	4.99	499	20.10	133	10.45	170	267
307	LN	4.44	444	19.55	129	9.95	162	245
308	LK	4.37	437	17.80	118	9.70	158	238
309	LP	4.79	479	18.95	125	10.32	168	257
310	LRP.C	4.41	441	16.20	107	10.22	166	236

A definite relation was found to exist between fertilizer treatment of the soils and residual effects on crop production in greenhouse pot tests. In general the variations in yields with different soil treatments was similar for all three crops. The relationship was especially noted for the sweet clover and soybean crops.

CARBON DIOXIDE PRODUCTION IN SOIL AFTER ADDITION OF ONE PER CENT PLANT MATERIAL PREVIOUSLY GROWN ON THE SOIL

Samples of soil from the pots used in the greenhouse tests were placed in the aspirating flasks used in the previous experiments for determining carbon dioxide production. The procedure described for the previous study of carbon dioxide production was followed. The results obtained both in milligrams and in per cent based on results from the untreated soil are shown in table 8.

The data show sweet clover to be more readily decomposed than soybeans

or rye. These results are in agreement with those of other workers. The explanation of this relationship has been thoroughly discussed in papers dealing directly with the subject and, hence, will not be repeated.

All soils receiving lime alone or lime plus fertilizer in the field produced more carbon dioxide from sweet clover than did the untreated soil. Likewise all treated soils with the exception of that receiving lime alone produced more carbon dioxide from soybeans than did the untreated soil. On the other hand, only soils 302 and 305 produced as much carbon dioxide from rye as did the untreated soil.

The soil receiving complete fertilizer in addition to lime produced more carbon dioxide from all three materials than did any other soil. This soil also produced the largest crops under both field and greenhouse tests.

A previous study showed marked differences in the power of these soils to produce carbon dioxide from cellulose. Only small differences, however, were

TABLE 8

Carbon dioxide produced from soils to which had been added plant tissue previously grown on them

SOIL		SWEET CLOVER		RYE		SOYBEANS		AVERAGE
Number	Field treatment	*mgm.*	*per cent*	*mgm.*	*per cent*	*mgm.*	*per cent*	*per cent*
301N	None	287	100	225	100	252	100	100
301S	Lime	296	103	200	89	262	99	99
302	LNPK	343	120	238	106	283	113	113
305	LPK	323	113	224	100	285	109	109
307	LN	320	111	216	96	282	106	106
308	LK	325	113	200	89	280	104	104
309	LP	309	108	211	94	289	105	105
310	LRP.C	295	103	201	89	286	102	102

found in the capacity of the soils to produce carbon dioxide from plant material grown on them, as indicated by the average results in table 8. It is evident, therefore, that addition of plant tissue, which contains all the nutritive elements, largely eliminates the differences in these soils, arising from previous treatment, to produce carbon dioxide.

A comparison of nitrification, carbon dioxide production, yields of crops, total nitrogen, and greenhouse studies is made in figure 2. Crop yields in the field and greenhouse, and carbon dioxide production from plant material show a close correlation for all soils except soil 309, which gave relatively higher yields in the greenhouse and in carbon dioxide produced from crops grown on it.

Nitrification, carbon dioxide production, both from cellulose and plant tissue, and greenhouse crop yields show a very close correlation in all soils but number 302, which gave relatively higher values in the greenhouse studies.

In general, it may be said that variations in crop producing power, resulting from previous soil treatment, correlate well with results of the studies of biological activities.

SUMMARY AND CONCLUSIONS

A study was made of changes in some of the more important chemical and biological conditions in a Fox sandy loam soil, resulting from fertilizer and lime applications over a period of 17 years. Particular emphasis was placed on crop production in relation to chemical and biological conditions in the soil and to field treatment.

The results permit of the following conclusions:

Lime plus complete fertilizer and lime plus phosphate and potash were the most effective in increasing the content of volatile matter of the soil and they also increased the nitrogen content, whereas all the other treatments decreased nitrogen content. Lime alone and lime plus individual nutrients increased the loss on ignition slightly.

All soil treatments increased pH values and available phosphorus.

All soil treatments increased crop yields, the lime plus complete fertilizer and lime plus phosphate and potash treatments being the most effective.

All soil treatments increased the number of fungi in the soil and greatly increased the number of bacteria. All fertilizer treatments in addition to lime proved beneficial to bacterial growth.

Nitrifying power of the soil varied greatly with the source of nitrifiable nitrogen. An average of results for alfalfa meal, cottonseed meal, diammonium phosphate, and urea showed that the two plots giving the highest crop yields and containing the largest content of volatile matter and a high content of available phosphorus to have the greatest nitrifying power.

All soil treatments except lime plus rock phosphate and gypsum increased the production of CO_2 from cellulose. Addition of $CaCl_2$ or KCl to soils receiving no field treatment decreased CO_2 production from cellulose, whereas Na_2HPO_4 and $NaNO_3$ increased it. CO_2 production in field treated soils, compared to that from untreated soil, was increased by addition of KCl, $CaCl_2$, or $NaNO_3$ but decreased by addition of Na_2HPO_4.

Yields of sweet clover, rye, and soybeans grown in jars of the different soils in the greenhouse correlated with yields obtained under field conditions. When the crop material grown on each jar was ground and an aliquot returned to a portion of the soil from the jar, CO_2 production correlated in general with crop yield.

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ABSORBED SODIUM IN SOILS AS AFFECTED BY THE SOIL-WATER RATIO

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Data are presented in this paper that bear on base exchange determinations and base exchange equilibria as affected by the soil-water ratio. The proportions as well as the absolute amounts of constituents found in 1:5 aqueous extracts of soils and in displaced soil solutions are very different. The neglect of this fact has given rise to misleading results in base exchange studies.

In 1928 the attention of one of us was attracted by a lemon grove near Chula Vista, California. This grove, since the time of its planting in 1897, has been irrigated exclusively from a dug well on the property. A water sample collected in 1928 contained 28 m.e. per liter (1,000 p.p.m.) of chloride, which is very high for an irrigation water and higher than any known to be used elsewhere for citrus irrigation. The initial and subsequent water samples from the well have been alike in that sodium has constituted approximately 50 per cent of the bases, magnesium has been a little less concentrated than calcium, and the bicarbonate and sulfate concentrations have been relatively low. The chloride concentration of the water from this well has varied upward from that of the initial sample to a chloride concentration of 44.35 m.e. (1,570 p.p.m.) in August, 1933. The trees in this grove are not in good condition.

Because of the recognition that this grove presented a subject of value in connection with salt-tolerance studies and that the concentration of chlorides in the soil solution of the root zone must at least approach the upper limit of citrus tolerance, soil samples were collected on December 8, 1933. These were taken both from the old grove (sample 239) and from a younger 10-year-old planting (sample 238) containing tangerines, grapefruit, and oranges, as well as lemons. Each of the samples represented the 6–24 inch horizon and was composited from five borings, including both the furrow area and the row centers. After the samples had been taken to the laboratory in moist condition and their moisture content increased with the well water, displacements of the soil solutions were made. Conventional 1:5 extracts were also made for comparison. The latter extracts were of oven-dried aliquots of the soils.

The analyses of these solutions brought to light outstanding differences between the proportions of sodium and calcium in the displaced soil solutions and in the 1:5 extracts (table 1). A much lower proportion of calcium was

[1] Rubidoux Laboratory, Riverside, California.

found in the 1:5 extracts than in the displaced solutions, whereas sodium was much higher in the extracts. These observations prompted further investigations including determinations of adsorbed bases and of the total exchange capacity of these soils. Upon the completion of this study six other soils of lesser salinity were similarly examined. One of these soils was further investigated after being wet with a solution containing about four times as much sodium, commercial NaCl, as there was calcium in the ammonium acetate extract. Five of these soils were from a series collected in 1931 for boron studies. Analyses of 5-times-saturation aqueous extracts of these five soils had been made previous to this inquiry.

The analytical procedures were those used at the Rubidoux Laboratory for water analyses. HCO_3, Cl, SO_4 were determined by the Official A. O. A. C. methods; Ca was determined by the titration of calcium oxalate; Mg, by weighing magnesium pyrophosphate; Na, by weighing uranyl zinc acetate hexahydrate; and K, by weighing di-potassium sodium cobaltinitrite monohydrate. Absorbed ammonia was determined by aeration by the Chapman and Kelley (2) procedure, following details of the method supplied by Dr. Chapman.

TABLE 1

Composition of displaced soil solutions and of 1:5 extracts

Concentrations are expressed in milligram equivalents per liter. Comparison of the displaced soil solutions and 1:5 extracts has been facilitated by multiplying the latter by appropriate factors which take account of the soil-water ratio, i.e., soil 238 by 27.9 (5/0.179) and soil 239 by 30.3 (5/0.165).

	Soil-water ratio	Milligram equivalents per liter							Sodium
		HCO_3	Cl	SO_4	Ca	Mg	K	Na	
									per cent
Soil 238:									
Displaced sol'n.....	1:0.179	4.0	285.6	18.2	92.0	76.5	22.2	144.0	49.7
1:5 ext. x 27.9.....	1:5	22.3	251.9	30.2	43.3	64.2	10.3	205.8	66.8
Soil 239:									
Displaced sol'n.....	1:0.165	3.8	219.0	14.2	68.8	69.8	6.7	92.4	41.7
1:5 ext. x 30.3.....	1:5	50.0	179.4	33.6	34.2	59.4	19.1	170.6	67.0

The Burd and Martin (1) procedure for the displacement of soil solution was followed, 2 kilos of soil packed in 2¼-inch displacement tubes being employed. Proebsting's (3) suggestion that the insides of the tubes be greased to prevent channelling was adopted, as was Hibbard's (5) scheme for automatically obtaining successive fractions of the displaced solution. At best, soil-solution displacements are difficult, and for successful displacements some exploratory work must ordinarily be carried out on each soil, such as variations in moisture content, firmness and method of tamping into the displacement tubes, and the amount of air pressure applied during displacement. If like conductances are obtained for several successive 20-ml. fractions of the percolate it is customary to assume that a true displacement has been obtained, but such conclusion may be in error. Channelling and displacement sometimes take place simultaneously at essentially uniform rates with misleading results. A further check on the adequacy of a displacement is accordingly required. The chloride content of an aliquot of displaced solution corresponding to 100 gm. of dry soil should be at least as high as that of a 1:5 extract of a corresponding soil mass. When a greater quantity of

chloride is represented by a displaced solution than by an aqueous extract the writers have concluded that a portion of the soil water has not functioned as a solvent and is not displaced, or, in other words, has behaved as bound water; possibly water of hydration of colloidal soil components. Accordingly, the *effective* soil moisture as represented by the displaced solution may be less than that represented by the moisture content of the soil as determined by drying at 105°C. (See footnote to table 2.) If our deduction with respect to the presence of *bound water* in certain of these soils is valid it would seem most logical to consider in this connection the water of hydration of SiO_2 and of the absorbed bases, particularly Na.

It has been found impossible to displace the soil solution from some heavy soils except at moisture contents well below the moisture equivalent percentage. If a soil is dispersed or is inclined to lose structure when handled moist it is advantageous to wet it by sprinkling uniformly after spreading to a uniform thickness of 5 mm. on a metal table top. When so spread and sprinkled, the soil is allowed to stand covered with an oilcloth overnight before it is mixed by sieving.

The observations made in the case of the Chula Vista soils were substantially confirmed by the analyses of the six additional soils (table 2). These findings may be stated as follows: *The amount of sodium, both relative and absolute, in the aqueous phase tends to increase as the water-soil ratio is increased, whereas the relative concentration of calcium (and magnesium in some cases) tends to decrease. The absolute amount of calcium in solution may remain unchanged or tend to increase with dilution when soils contain an excsss of sparingly soluble salts such as $CaCO_3$ or $CaSO_4$.*

This phenomenon cannot be explained on the basis of solubility. On that basis it would be expected that Ca and Mg rather than Na and K would appear in the aqueous phase with dilution, since, with the exception of the chlorides, Ca and Mg salts are less soluble than the corresponding salts of Na and K. It would be equally difficult to explain it as due to the hydrolysis of Na of the absorbing complex, since the concentration of other salts in solution was probably sufficiently high to minimize such hydrolysis. Hydrolysis in the soils examined likewise would fail to account for the disappearance of Ca from the aqueous phase with dilution. *The most satisfactory explanation of this phenomenon is that a cation exchange reaction takes place when the water : soil ratio is increased whereby calcium enters the absorbing complex and sodium is liberated.*

From 4 to 17 times as much bicarbonate (alkalinity to methyl orange reported as bicarbonate) was found in 1:5 extracts as in the displaced soil solutions. As previously stated, it would not be reasonable to connect all of this increase with hydrolysis of the adsorbed Na. Electrometric determinations of pH with a glass electrode (for which we are indebted to L. V. Wilcox) were made only in the case of soil 277. The pH values for the soil:water ratios 1:0.117, 0.154, 0.5, 1.0, 2.5, 5.0, 10.0 were respectively as follows: 7.48, 7.31, 7.60, 7.24, 7.02, 6.97, 6.97. In the case of the remaining soils colorimetric pH determinations did not show significant trends or variations. The increase in HCO_3 was probably due for the most part to the carbonates of Ca and Mg entering the solution. The cations, Ca and Mg, which entered

TABLE 2

Cations of displaced soil solutions, 5 times saturation extracts, 1:5 extracts, and ammonium acetate extracts

SOIL NO.	MOISTURE EQUIVALENT	SOIL WATER RATIO	MILLIGRAM EQUIVALENTS PER 100 GM. SOIL									PER CENT OF TOTAL			
			HCO_3	Cl	SO_4	Ca	Mg	K	Na	Total bases	NH_4 absorbed	Ca	Mg	K	Na
	per cent														
238*	20.7	1:01.79	0.06	4.50	0.29	1.45	1.21	0.35	2.27	5.28	.....	27	23	7	43
		1:2.325	0.34	4.48	0.42	0.94	1.12	0.10	3.31	5.47	.....	17	21	2	60
		1:5	0.40	4.51	0.54	0.78	1.15	0.18	3.69	5.80	.....	13	20	3	64
Ammonium acetate extract						9.06	7.88	1.02	4.53	22.49	22.31				
239*	23.4	1:0.165	0.05	2.90	0.18	0.92	0.92	0.09	1.22	3.15	.....	29	29	3	39
		1:2.700	0.46	2.84	0.35	0.61	0.71	0.06	2.40	3.78	.....	16	19	2	63
		1:5	0.83	2.96	0.55	0.56	0.98	0.31	2.82	4.67	.....	12	21	7	60
Ammonium acetate extract						19.01	10.55	1.11	3.93	34.60	18.59				
2	11.9	1:0.123	0.08	0.13	0.15	0.29	0.09	0.02	0.19	0.59	.....	49	15	3	33
		1:1.565	0.39	0.11	0.15	0.35	0.13	0.05†	0.34	0.87	.....	40	15	6	39
		1:5	0.89	0.13	....	0.50	0.22	0.11	0.43	1.26	.....	40	17	9	34
Ammonium acetate extract						36.34	2.43	0.55	0.77	40.09	8.82				
4	11.5	1:0.122	0.14	0.06	0.09	0.17	0.07	0.01	0.09	0.34	.....	50	21	3	26
		1:1.415	0.27	0.07	0.11	0.21	0.11	0.03†	0.19	0.54	.....	39	20	6	35
		1:5	0.59	0.09	....	0.42	0.27	0.04	0.27	1.00	.....	42	27	4	27
Ammonium acetate extract						9.04	1.06	0.90	0.99	11.99	8.34				
4A*	....	1:0.124	....	31.69	....	3.89	0.98	0.11	29.84	34.82	.....	11	3	..	86
		1:5	....	31.69	....	2.02	0.64	0.14	32.40	35.20	.....	6	2	..	92
Ammonium acetate extract						8.70	3.65	2.20	32.55	47.10	8.33				
7	22.5	1:0.174	0.06	0.18	0.69	0.45	0.25	0.01	0.30	1.01	.....	45	24	1	30
		1:2.340	0.33	0.15	0.91	0.46	0.27	0.01†	0.69	1.43	.....	32	19	1	48
		1:5	0.57	0.17	0.75	0.48	0.72	0.02	0.81	2.03	.....	24	35	1	40
Ammonium acetate extract						15.96	7.06	0.46	1.51	24.99	18.70				

* On the assumption that all of the chloride of soils 238, 239, and 4A was in solution in the 1:5 extracts, the chloride found in the displaced soil solutions of these soils corresponded respectively to 15.8, 13.5, and 11.4 ml. of water per 100 gm. of soil rather than to the 17.9, 16.5, and 12.3 ml. as represented by moisture determinations on aliquots of the soil as packed. The concentrations of all displaced solution constituents of these three soils accordingly are calculated to 100 gm. of dry soil on the basis of the active water indicated by the chloride determinations.

† Determined by difference in 1931.

TABLE 2—*Concluded*

SOIL NO.	MOISTURE EQUIVALENT	SOIL WATER RATIO	MILLIGRAM EQIVALENTS PER 100 GM. SOIL									PER CENT OF TOTAL			
			HCO_3	Cl	SO_4	Ca	Mg	K	Na	Total bases	NH_4 absorbed	Ca	Mg	K	Na
	per cent														
9	17.4	1:0.127	0.05	0.35	0.56	0.58	0.36	0.01	0.22	1.17	.....	50	31	1	18
		1:1.785	0.26	0.31	1.16	0.79	0.49	0.09†	0.58	1.95	.....	40	25	5	30
		1:5	0.84	0.36	0.98	0.81	0.60	0.07	0.77	2.25	.....	36	27	3	34
Ammonium acetate extract						11.99	5.44	1.11	0.91	19.45	14.79				
10‡	21.3	1:0.144	0.04	0.48	1.38	0.38	0.23	0.02	1.41	2.04	.....	19	11	1	69
		1:2.215	0.43	0.54	2.27	0.31	0.30	....	2.84	3.45	.....	9	9	..	82
		1:5	0.62	0.55	2.47	0.41	0.30	0.16	3.13	4.00	.....	10	7	4	79
Ammonium acetate extract						10.49	10.06	0.94	5.22	26.71	15.30				
277	16.8	1:0.117	0.07	0.48	0.11	0.24	0.07	Tr.	0.35	0.66	.....	36	11	..	53
		1:0.154	0.06	0.50	0.10	0.21	0.07	....	0.43	0.71	.....	30	10	..	60
		1:0.5	0.14	0.44	....	0.14	0.06	....	0.48	0.68	.....	21	9	..	70
		1:1.0	0.19	0.46	0.18	0.15	0.09	....	0.61	0.85	.....	18	10	..	72
		1:2.5	0.37	0.48	0.23	0.19	0.11	....	0.79	1.09	.....	17	10	..	73
		1:5.0	0.57	0.46	....	0.20	0.10	Tr.	0.86	1.16	.....	17	9	..	74
		1:10.0	0.74	0.48	0.21	0.21	0.14	....	0.95	1.30	.....	16	11	..	73
Ammonium acetate extract.....						12.45	4.25	1.85	2.31	20.86	12.74				

‡ Repeated trials for a better displacement of soil 10 at the time of the above work were unsuccessful. Subsequently, by the use of a long 1-inch displacement tube and a conical tamper, a solution was obtained that had a chloride content corresponding to 0.84 m.e. per 100 gm. of soil, indicating 5.0 ml. of bound water per 100 gm. of soil. Channelling to the extent of 43 per cent in the displaced solution of soil 10 as reported in this table is indicated by the 0.84 m.e. of chloride found in this subsequent displacement. This channelling a little more than offsets the bound water, but corrections have not been applied to the data.

In these deductions with respect to bound water, recognition has not been given to the possibility that chloride, at least to a limited extent, may be adsorbed. If chloride was adsorbed in these cases then our bound water estimates are too low.

with dilution as carbonates or bicarbonates, however, replaced in part Na of the absorbing complex and in part remained in solution. The presence in the soil of sparingly soluble salts such as $CaCO_3$ and $CaSO_4$ tends to obscure the base exchange effect because the quantity of Ca derived from these salts increases with the proportion of solvent used.

If the energy of absorption of Ca, Mg, K, and Na from aqueous solutions decreases in the order named, calcium should displace sodium to the greatest extent, which is the result observed. In a number of cases appreciable quantities of magnesium appeared in the aqueous phase with dilution. To what extent this magnesium was displaced by calcium or derived by the solution of $MgCO_3$ is uncertain. The liberation of Mg from the absorbing complex by

Ca displacement should follow, if not accompany, Na displacement, particularly when the concentration of adsorbed sodium is relatively low. In the soils here examined relatively little potassium was displaced by ammonium acetate; the actual and relative amounts were less than of sodium. The relative concentrations of the four bases in the aqueous and solid phases are functions of their energy of absorption and of their thermodynamic activities. Vanselow (7) has assumed the thermodynamic activities of the cations in the solid phase to be equal to their mol fractions, since he considers the solid phase to be a solid solution or mixed crystal.

Two distinct effects are made evident by the data of table 2. Both are important and both simultaneously contribute to the reclamation of calcareous alkali soils when leached with non-saline waters. The first of these effects for convenience may be designated as the *calcium carbonate effect* and the second as the *dilution effect.*

The calcium carbonate effect has come to be generally recognized. Experiments and discussion by Kelley and Brown (6), Gedroiz (4), and others may be referred to. When the soil solution of a calcareous alkali soil is replaced by non-saline water, Ca comes into solution from solid $CaCO_3$ and the proportion of Ca in the aqueous phase is thereby momentarily increased. With this increase in the concentration of Ca relative to Na, absorbed Na is replaced and continues to be replaced by more Ca from $CaCO_3$ until the Ca and Na of the aqueous phase are in equilibrium with the Ca and Na of the absorbed phase. At equilibrium the aqueous phase is higher in Na than in Ca, since the energy of absorption of the latter is the greater. Reclamation is effected when the cycle has been repeated until Na of the exchange complex has been largely replaced by Ca derived from $CaCO_3$.

The dilution effect as here demonstrated has implications of a broader nature but it likewise contributes to the effectiveness of reclamation by leaching though its significance in this connection seems not to have been elaborated. Dilution of the aqueous phase *per se* causes a shift in the equilibrium concentrations of Ca and Na in the liquid and solid phases. If the liquid phase is diluted, as by adding distilled water, Ca enters the exchange complex from solution and displaces Na, i.e., by this exchange the relative concentration of Ca is decreased in the aqueous phase and increased in the exchange complex and the bases replaced by Ca accordingly appear in the aqueous phase.

The effect of dilution upon the exchange equilibrium is clearly illustrated by both soils 238 and 239 (table 1 and 2). The absolute as well as the relative amount of Ca of the aqueous phase of both of these soils is decreased in the order of 50 per cent by 27.9- and 30.3-fold dilutions. The principle could be more clearly shown with saline non-calcareous soils, since even in these two soils a part of the Ca replacing Na of the exchange complex was derived from solid $CaCO_3$ or $CaSO_4$ (note that the Na increase exceeds the HCO_3 plus SO_4 increase). In the other soils the effect of dilution upon the absolute amount of calcium in the aqueous phase is largely masked, but as shown in table 4 the

sodium percentages in the aqueous phase of the 1:5 extracts of all soils exceeded the sodium percentages of the displaced soil solutions. It is likewise shown that for each of these soils the sodium percentage of the exchange complex was lower when in equilibrium with 1:5 extracts than when in equilibrium with the soil solution.

If Vanselow's (7) equation G for exchange equilibrium is the correct one, the dilution effect may be mathematically stated for a system containing two active bases and a single active exchange substance. In soils the system is of course a complicated one, since several bases participate and there are present both organic and inorganic materials of complex character that possess base-exchange properties.

$CaCO_3$ and $CaSO_4$ have been emphasized as the important sources of the Ca entering the aqueous phase. It must be recognized, nevertheless, that Ca as well as other bases, including Na, may be derived to a limited extent from other slightly soluble soil constituents.

In the light of the foregoing it becomes apparent that the practice of determining adsorbed sodium and potassium in the soil by subtracting the "water-soluble" Na and K of 1:5 extracts from the total Na and K as found for example in ammonium acetate extracts may result in serious error if the investigator assumes that his results represent the facts as they apply to soils with ordinary field moisture. Values for exchangeable Ca and Mg obtained by subtracting exchangeable Na and K from the total exchange capacity of a soil must also be subject to error if the exchangeable Na and K are not correctly estimated.

In table 3 we have set forth the amounts and percentages of exchangeable bases in the nine soils as ordinarily computed on the basis of Na and K in 1:5 extracts, and also as computed on the basis of the displaced soil solution. Sodium and potassium of the aqueous phase are subtracted from the ammonium-displaced Na and K, and the differences are recorded as replaceable Na and K. The sum of replaceable Na and K is then subtracted from the value for ammonia by aeration and recorded as exchangeable Ca plus Mg. These results show that exchangeable sodium as estimated on the basis of 1:5 extracts may be less to the extent of 50 per cent or more than that estimated on displaced solutions.

It has seemed pertinent to examine these data further to ascertain what relationships might exist between the proportions of bases in the aqueous and absorbed phases. The results of this inquiry are presented in table 4. In this table the sodium percentages of the liquid phases are from table 2; and those of the absorbed phases, from table 3. The corresponding alkali base percentages in the two phases have been calculated by combining sodium and potassium. Total bases of the liquid phase in terms of milligram equivalents per liter are taken from the original work sheets. The latter column, like the total-exchange-capacity column, has been introduced to facilitate comparisons of total bases with the equilibrium ratios presented in the two columns at the

right. Percentage of alkaline earth bases (calcium plus magnesium) is not shown as it is conversely dependent upon percentage of alkali bases.

When the variability in the kind and proportion of mineral and organic substances that may make up the absorbing phase of a soil and the number of cations involved are recognized it is perhaps not surprising that in these diverse soils the ratios between the sodium percentage in the displaced solution and that of the absorbed phase have varied by as much as that represented by the

TABLE 3

Replaceable cations calculated on basis of displaced soil solutions and on basis of 1:5 extracts

	MILLIGRAM EQUIVALENTS PER 100 GM. SOIL			Na AS PER CENT TOTAL	Na + K AS PER CENT TOTAL
	Ca + Mg	K	Na		
Soil 238:					
Displaced sol'n	19.38	0.67	2.26	10	13
1:5 extract	20.53	0.84	0.84	4	8
Soil 239:					
Displaced sol'n	14.86	1.02	2.71	15	20
1:5 extract	16.68	0.80	1.11	6	10
Soil 2:					
Displaced sol'n	7.71	0.53	0.58	7	11
1:5 extract	8.04	0.44	0.34	4	9
Soil 4:					
Displaced sol'n	6.55	0.89	0.90	11	21
1:5 extract	6.76	0.86	0.72	9	19
Soil 4A:					
Displaced sol'n	3.53	2.09	2.71	33	58
1:5 extract	6.12	2.06	0.15	2	27
Soil 7:					
Displaced sol'n	17.04	0.45	1.21	6	9
1:5 extract	17.56	0.44	0.70	4	6
Soil 9:					
Displaced sol'n	13.00	1.10	0.69	5	12
1:5 extract	13.61	1.04	0.14	1	8
Soil 10:					
Displaced sol'n	10.57	0.92	3.81	25	31
1:5 extract	12.43	0.78	2.09	14	19
Soil 277:					
Displaced sol'n	10.78	Tr.	1.96	15	15
1:5 extract	11.29	Tr.	1.45	11	11

2.4 to 5.0 range. The corresponding alkali base ratios vary from 1.3 to 3.8. The sodium percentages of the aqueous phase of the soils extracted with five times their weight of water were from 3 to 46 times the corresponding sodium percentages of the absorbed phase. In all cases dilution served to increase the proportion of sodium in the aqueous phase and to decrease the proportion in the absorbed phase. As judged by these data it seems improbable that a mathematical relationship applicable to all soils can be established for the effect of dilution on absorbed base equilibria in complex soil systems.

The percentage of sodium in natural waters $\left(\frac{Na \times 100}{Ca + Mg + Na}\right.$, concentrations in milligram equivalents) is now recognized by this laboratory as an important characteristic of irrigation water. This recognition results from the observation that when lands are irrigated with waters having high sodium percentages they commonly become deflocculated and impervious. The rapidity with which such effects become apparent is contingent not only upon the total salinity of the water but upon the character of the soil irrigated. It is believed

TABLE 4

Ratios of relative concentrations of bases in the aqueous and absorbed phases

SOIL	LIQUID PHASE			ABSORBED PHASE			Na IN SOL'N / Na ABSORBED	AB IN SOL'N / AB ABSORBED
	Total bases	Total sodium	Total alkali bases	Total exchange capacity	Total sodium	Total alkali bases		
	Displaced soil solutions							
	m.e./liter	*per cent*	*per cent*	*m.e./100 gm. soil*	*per cent*	*per cent*	*per cent*	*per cent*
238	334.7	43	50	22.31	10	13	4.3	3.8
239	237.7	39	42	18.59	15	20	2.6	2.1
2	47.6	33	35	8.82	7	11	4.7	3.1
4	27.7	26	29	8.34	11	21	2.4	1.3
4A	3064.6	86	87	8.33	33	58	2.6	1.5
7	57.7	30	30	18.70	6	9	5.0	3.4
9	91.6	18	19	14.79	5	12	3.6	1.6
10	141.9	69	70	15.30	25	31	2.8	2.3
277	56.8	53	53	12.74	15	15	3.5	3.5
	1:5 extracts							
238	11.59	64	67	22.31	4	8	16.0	8.4
239	9.35	60	67	18.59	6	10	10.0	6.5
2	2.53	34	43	8.82	4	9	8.5	4.9
4	1.98	27	31	8.34	9	19	3.0	1.6
4A	70.37	92	92	8.33	2	27	46.0	3.5
7	4.09	40	41	18.70	4	6	10.0	6.7
9	4.51	34	37	14.79	1	8	34.0	4.6
10	7.99	79	82	15.30	14	19	5.6	4.4
277	2.29	74	75	12.74	11	11	6.6	6.6

by some, a viewpoint subscribed to by the writers, that this tendency toward deflocculation and impermeability and ultimate unproductiveness is the result of the gradual replacement by sodium of a part of the Ca and Mg of the exchange complex of the soil. Many deflocculated soils are rendered permeable when treated with calcium sulfate. Such observations have supported the base-exchange explanation, but determinations of exchangeable sodium based on 1:5 extracts have generally shown very little sodium in the absorbing complex; sometimes, in fact, an absence of this element is indicated, which is in-

conceivable when substantial concentrations of Na are present in aqueous extracts. Such observations have caused some investigators to doubt the adequacy of the absorbed-sodium interpretation of soil impermeability. The incentive to interrupt other investigations to follow the suggestion afforded by the Chula Vista soils was the possibility that some advancement in the reliability of measuring exchangeable sodium and therefrom a better understanding of the irrigation-water effect might result.

Attention is directed to the data of tables 1 and 2 to illustrate and emphasize an important soil-water relationship; namely, *If we regard solutions displaced from soils as representative of the soil solution, then the significance of more dilute aqueous extracts becomes highly questionable. Only occasionally is it possible to convert the concentrations of constituents found in the dilute aqueous extracts to concentrations as of the soil solution with reasonable accuracy.* The quantity of bicarbonate obtained by aqueous extraction of soils containing carbonate is far greater than that represented in displaced soil solutions. The sulfate obtained by aqueous extraction may exceed that found by displacement; adsorption as well as the limited solubility of calcium sulfate is believed to contribute to this effect. A fair notion of chloride and nitrate concentrations in the soil solution can sometimes be obtained from aqueous extracts, but the bound-water effect may cause the soil solution as presented to the plant to be considerably more concentrated than expected. The proportions and absolute amounts of bases in water extracts are quite different from those of displaced solutions.

Serious manipulative difficulties are admittedly inherent to the present method of displacing the soil solution from different soils. The soil-solution approach to the study of some phases of plant nutrition, salt tolerance, and soil behavior problems as presented under field conditions, however, offers such promise that the displacement procedure becomes deserving of much patient study with a view toward the improvement of its workability as applied to all soils. Recent advances in the development of microanalysis offer promise in this connection, since a material reduction in the quantity of solution required in the laboratory would minimize some of the difficulties.

SUMMARY

The proportion and absolute amount of sodium (usually magnesium and potassium also), represented in aqueous extracts of soils are found to be higher than those represented in displaced soil solutions. The proportion (sometimes the absolute amount) of calcium is lower in extracts than in displaced solutions. This release of Na with dilution cannot be ascribed to hydrolysis, and hydrolysis would fail to account for the decrease in Ca. The most satisfactory explanation of this phenomenon is that a cation-exchange reaction takes place when the water-soil ratio is increased. In this exchange, calcium enters the absorbing complex and sodium (sometimes magnesium and potassium) is liberated. New Ca coming into solution from $CaCO_3$ and $CaSO_4$ with dilution tends to obscure the Ca absorption effect in many soils.

The assumption that Na of aqueous extracts represents Na in the aqueous phase at field moisture appears to be untenable, and accordingly the practice of determining absorbed Na by deducting aqueous-extract Na from ammonium-extract Na may lead to erroneous results. Exchangeable sodium as estimated on the basis of 1:5 extracts may be less than that estimated on displaced solutions to the extent of 50 per cent or more.

The percentage of sodium (as of total bases) in displaced solutions was greater than the percentage of sodium absorbed (corrected on basis of displaced solutions) by 2.4 to 5.0 times. The percentage of sodium of 1:5 extracts exceeded the percentage of sodium absorbed (corrected on basis of 1:5 extracts) by 3 to 46 times.

Bicarbonate as represented by 1:5 extracts of the nine soils was 4 to 17 times greater than that represented by displaced solutions. Sulfate tended to increase with dilution. This increase is ascribed in part to $CaSO_4$ coming into solution and in part to SO_4 adsorption at field moisture. Certain soils gave higher absolute amounts of chloride by displacement than by 1:5 extracts; this is attributed to bound water in the soil, i.e., water not functioning as a chloride solvent and not released during displacement.

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ESTIMATION OF REPLACEABLE Na AND K, EXCHANGE CAPACITY, AND DEGREE OF ALKALIZATION IN ALKALI SOILS BY AMMONIUM CARBONATE EXTRACTION

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The writer has recently advocated the use of $Ba(OH)_2$ for the estimation of exchangeable Na and K in soils (1). The same reagent is employed for finding exchange capacity (2) and degree of alkalization (3) of soils. The use of $Ba(OH)_2$ simplifies the estimation to a single titration, and, unlike neutral salt replacement, the preliminary leaching to remove soluble salts is not necessary. Preliminary leaching was, however, required in the case of soils containing alkali sulfates, as these could react with $Ba(OH)_2$, producing NaOH, which introduced a positive error in the estimation. It appeared, however, that ammonium carbonate would be free from this objection. As will be seen from what follows, this reagent proved superior to $Ba(OH)_2$ in more than one way for the purpose for which the latter was advocated.

EXPERIMENTAL

Replaceable Na and K by the $Ba(OH)_2$ method

This method has already been fully described (1). Briefly it consists in leaching the soil with 1,000 cc. of 0.1 *N* $Ba(OH)_2$; passing CO_2 through the leachate; and evaporating down 500 cc. of the supernatant liquid, followed by extraction of the residue with dilute ammonia when Na and K carbonates are dissolved and estimated by titration after boiling to remove ammonia.

Exchange capacity

The soil is saturated with Na by leaching with NaCl; the exchangeable Na is then determined by leaching with $Ba(OH)_2$.

Degree of alkalization

Degree of alkalization (D.A.) is defined as the percentage of monovalent bases (Na and K) on the total exchange capacity of the soil. The usefulness of D.A. values for characterising alkali soils has already been discussed elsewhere (3).

[1] *Editor's note:* At the author's request, the order of publication of this paper and of one received October 9, 1934 has been reversed.

Ammonium carbonate method

Ten to twenty grams of soil are leached with 500 cc. of 0.2 *N* $(NH_4)_2CO_3$ in 100-cc lots. The leachate is evaporated to dryness on a hot plate or in an air oven. The residue is taken up with 50 per cent alcohol and filtered. The filtrate is evaporated to dryness and titrated against standard acid after some water has been added. The titration value gives the amount of exchangeable Na and K in the soil. The titration is more satisfactorily done by adding excess of standard acid and back titrating with standard alkali after boiling the solution to drive away CO_2 and using brom thymol blue as indicator. For the purpose of the present investigation it was not considered necessary to determine K separately. The exchangeable Na and K are therefore recorded together.

Exchange capacity was measured on the same sample after the $(NH_4)_2\ CO_3$ treatment by leaching the soil with 500 cc. of *N* NaCl or 0.2 *N* KCl in 100-cc. lots, followed by leaching with 0.2 *N* $(NH_4)_2CO_3$ as described in the foregoing, with the modification that the residue is taken up with a little hot water instead of 50 per cent alcohol and titrated directly after filtration. Degree of alkalization was calculated by the formula

$$\text{D. A.} = \frac{n\ 100}{N}$$

Where n = m. equivalents of replaceable Na and K and N = exchange capacity in m. equivalents.

Comparison with the $Ba(OH)_2$ method

In order to prove the utility of the ammonium carbonate method it was necessary to compare it with the $Ba(OH)_2$ method that has already been found to give good results. For this purpose 37 soils were chosen at random from a farm of 600 acres. The idea was to select fields of widely divergent characteristics as regards yield. The results are recorded in table 1. A column giving the yield of rice or barley is also included to show the significance of D.A. values. It is not intended to bring out a strict correlation between D.A. values and yield, because not only were the soils of different series, but the crops were different. Besides, the samples were taken some time after the crop had been harvested when the soil could be expected to have undergone a good deal of change. The general trend of results, however, would serve the purpose of emphasizing the usefulness of characterizing alkali soils on the basis of D.A. values. A much better correlation between the D.A. and yield will be brought out in another series described later.

It will be seen from table 1 that the two methods of finding exchangeable Na and K in soils agree fairly well when the fact that sampling errors must have caused some divergence is considered. The $(NH_4)_2\ CO_3$ method is simpler and more accurate than the $Ba(OH)_2$ method, because, in the former,

TABLE 1

Comparison of the $Ba(OH)_2$ and $(NH_4)_2CO_3$ methods for replaceable Na and K, exchange capacity, and degree of alkalization

LAB. NO.	EXCHANGEABLE Na AND K		EXCHANGE CAPACITY		DEGREE OF ALKALIZATION		YIELD OF RICE OR BARLEY PER ACRE
	$Ba(OH)_2$ method	$(NH_4)_2CO_3$ method	$Ba(OH)_2$ method	$(NH_4)_2CO_3$ method	$Ba(OH)_2$ method	$(NH_4)_2CO_3$ method	
	m.e.	*m.e.*	*m.e.*	*m.e.*	*per cent*	*per cent*	*lbs.*
Rice soils:							
172	4.40	3.55	7.6	7.35	57.9	48.3	205
166	6.70	6.40	8.40	8.30	79.8	77.1	266
168	4.46	3.85	6.64	6.05	67.2	63.6	410
171	5.96	5.70	9.50	9.25	62.7	61.6	451
164	8.70	8.75	9.72	10.50	89.5	83.3	533
162	7.20	6.70	11.30	10.05	63.7	66.7	615
170	3.10	3.90	6.70	6.70	46.3	58.2	656
159	5.90	5.65	7.80	8.50	75.6	66.5	738
167	5.34	4.45	8.40	8.00	63.6	55.6	984
160	8.68	9.00	11.20	10.80	77.5	83.3	1,066
163	8.00	6.80	7.82	8.10	100.0	84.0	1,230
165	4.08	4.55	6.84	7.10	59.6	64.1	1,394
157	6.20	6.50	9.00	8.90	68.9	73.0	1,476
158	3.76	3.00	9.28	7.74	40.5	38.8	1,558
169	2.90	2.90	6.94	6.60	41.8	43.9	1,640
155	5.20	5.20	10.48	8.45	49.6	61.5	1,722
161	5.40	4.80	8.40	8.30	63.7	57.8	1,968
156	7.30	7.75	10.30	9.70	70.9	79.9	2,090
153	2.20	1.95	9.50	8.70	23.6	22.4	2,214
154	1.40	1.00	5.82	5.60	24.1	17.9	2,542
174	2.84	2.40	6.47	6.65	43.9	36.1	2,952
173	2.80	2.40	9.70	8.35	28.8	28.7	3,280
Barley soils:							
179	4.00	3.60	5.40	4.50	74.1	80.0	117
190	2.26	2.10	6.20	6.55	36.4	32.1	122
187	5.70	5.50	10.40	8.90	54.8	61.8	124
188	5.52	6.05	7.70	5.80	71.7	100	161
177	8.40	10.50	10.18	10.60	82.5	99.0	161
176	6.64	5.35	7.80	7.20	85.1	74.3	206
175	4.20	3.95	6.70	7.00	62.7	56.4	283
184	5.18	4.70	7.58	6.70	68.3	70.2	310
185	9.80	8.70	11.20	10.50	87.5	82.8	328
180	5.78	5.95	8.80	8.95	65.7	66.5	431
181	5.72	5.55	9.28	7.00	61.6	79.3	457
178	3.00	2.90	8.80	8.90	34.1	32.6	584
186	1.62	1.65	5.30	4.40	30.6	37.5	638
183	5.60	4.70	7.18	6.25	78.0	75.2	706
182	1.32	0.45	4.42	3.5	29.9	12.9	1,038

the whole of the filtrate is evaporated down and the titration directly gives the total exchangeable Na and K in the soil. Another advantage is that the method can be used in the presence of sulfates, which interfere with the $Ba(OH)_2$ method.

For finding exchange capacity the use of NaCl was advocated in a previous paper (2). Subsequent work has shown that KCl is equally good and has the advantage that a 0.2 *N* solution serves the same purpose as a normal solution of NaCl, and, besides, only 500 cc. of the solution is required for completely saturating the soil with K, which is subsequently determined by replacement with $(NH_4)_2\,CO_3$ just as easily as is Na from the sodium-saturated soil. The values for exchange capacity given in table 1 were obtained by NaCl leaching in one case and KCl in the other. Their general agreement indicates

TABLE 2

Relation between degree of alkalization [$(NH_4)_2CO_3$ Method] and yield of wheat in Montgomery soils

SOIL NO.	CULTURAL TREATMENT	n*	N†	D.A.‡	YIELD OF WHEAT GRAIN PER ACRE
		m.e.	*m.e.*	*per cent*	*lbs.*
1	Control I	3.72	5.20	71.5	309
2	Control II	6.38	6.95	91.8	32
3	Flooding and washing I	4.45	5.10	87.3	428
4	Flooding and washing II	4.70	6.75	69.6	69
5	$CaCl_2$, 1 ton per acre	2.45	5.30	46.2	627
6	$CaCl_2$, 1.5 tons per acre	1.33	5.60	23.7	1004
7	$CaCl_2$, 2 tons per acre	1.55	5.95	26.0	1146
8	Gypsum, 1 ton per acre	1.25	5.20	24.0	852
9	Gypsum, 1.5 tons per acre	1.73	6.40	27.0	451
10	Gypsum, 2 tons per acre	2.50	5.60	44.6	766

* n = Replaceable Na and K.
† N = Exchange capacity.
‡ D.A. = Degree of alkalization.

that either NaCl or KCl can be used, the choice of the latter being a matter of convenience.

The usefulness of D.A. values is brought out in a striking manner in another series of soils from Montgomery District where reclamation experiments were being conducted. These results are given in table 2, which also includes a column showing the cultural treatment received by each plot. It will be seen that the D.A. values generally run according to what one might reasonably expect from the cultural treatment. Determination of D.A. values, therefore, would help in following the course of reclamation in alkali soils.

SUMMARY

The use of ammonium carbonate for the estimation of replaceable Na, K, exchange capacity, and degree of alkalization is advocated. The proposed

method is shown to be simpler than the writer's $Ba(OH)_2$ method and can be used without subjecting the soil to a preliminary leaching to remove soluble salts.

The usefulness of degree of alkalization determination for characterizing alkali soils is discussed.

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THE LAWS OF SOIL COLLOIDAL BEHAVIOR: XVII. MAGNESIUM SILICATE—ITS BASE-EXCHANGE PROPERTIES[1]

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Very few soil investigations have offered more fundamental data on the make-up of soil and on the intricate problems of soil fertility than the researches on the composition and structure of the soil silicates. The foundation of these researches was laid by Van Bemmelen (2), and these have been followed up throughout the world. In recent years, with the advances made in the realm of colloid chemistry, a closer approach has been made in the study of a number of silicate systems, particularly those of iron and aluminum.

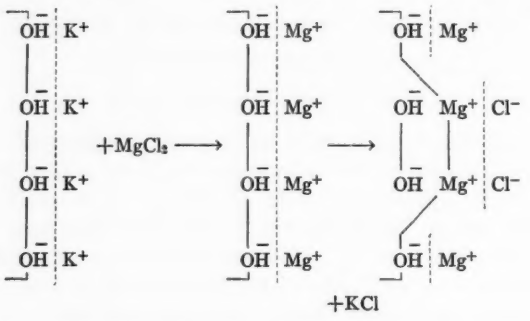
This led to the study of other silicate systems. A number of observed facts on magnesium in plant physiological reactions, on its peculiar mode of movement and translocation in the soil profile, and on its behavior in the exchange complex of the soil, have made the Mg-silicate system of particular interest. A few of these facts, primarily those pertaining to soils, are reviewed before the experimental data on this problem are presented.

In the case of electrodialytic phenomena, the Mg naturally present in soil colloids acts more like Fe and Al than like Ca or the alkali metals. That is, Mg becomes mobile only after the bulk of the other cations of the strong bases, Ca, K, and Na, have been removed. At the same time Mg is displaceable from a neutral soil by the neutral salt treatment, whereas Fe and Al are not. This phenomenon was described by Oden and Löddesöl (15), Löddesöl (9), and Mattson (11). Kelley, Dore, and Brown (8), investigating the base-exchange properties of bentonites, which are primarily crystalline Mg-aluminum silicates, have shown conclusively that if the natural colloid be sufficiently ground, practically all of the Mg can be made exchangeable. Anderson and Mattson (1) found that the "non-exchangeable" cations present in the natural colloids made up a general average of about two-thirds to three-fourths of the total mono- and divalent bases present. Later Mattson (12), in the light of the work of Kelley, Dore, and Brown, agreed that the cations are non-exchangeable because of their position within the crystal lattice or molecular aggregates. Mattson (13) and Löddesöl (9) both found, however, that if an electrodialyzed soil colloid is saturated by treatment with MgO alone, the Mg is released in a manner similar to the manner of release of the Ca and the alkali metals, but at the same time only about half of the Mg added can be released again by electrodialysis.

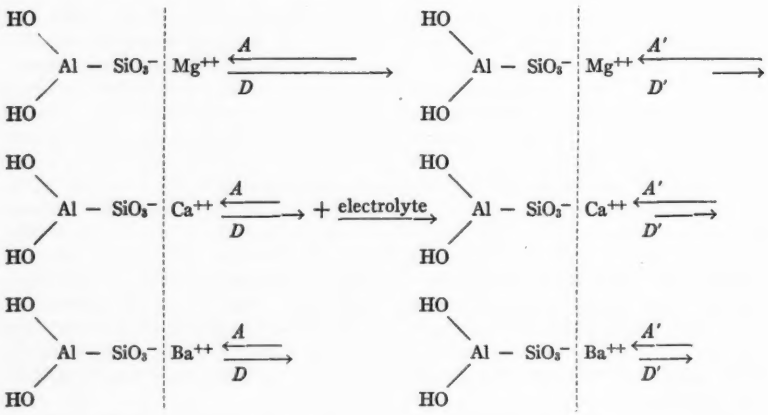
Wiegner and Jenny (20) made the important observation that whereas the displacing power of the divalent cations places them in the normal lyotropic order, Mg < Ca < Ba, the ease with which these cations are displaced when once in combination with the complex is

[1] Journal Series paper of the New Jersey Agricultural Experiment Station, department of soil chemistry and bacteriology.

Mg < Ca < Ba, that is, the Mg is the most difficult to replace as measured against the NH_4 ion. This condition is anomalous as compared to the lyotropic order and the order of ease of replacement of the alkali cations. Wiegner and Jenny ascribe this phenomenon to the solubility of the hydroxides, which is $Ba(OH)_2 > Ca(OH)_2 > Mg(OH)_2$, i.e., the inner layer of anions consists partly of OH^- ions which bind the Mg more firmly. Jenny (5) pictures the seat of the exchange in a Helmholtz double layer in which the inner layer consists chiefly of OH^-, explaining the "anomalous" behavior of the Mg by the following diagram:



Mattson (13), however, states that Wiegner and Jenny's explanation is insufficient to account for the anomaly, since sesquioxides combine with bases only at pH values above their isoelectric point; however, the introduction of SiO_2 or other acidoid renders the complex exchange active far over on the acid side of pH 7.0. The bond between cation and complex therefore must be through the silicate group, and the seat of the cation adsorption and exchange is in the free valencies of the silicate anion. Mattson (13) suggests a mechanism which may be diagrammatically represented[2] as follows:



Free colloid

[2] The lengths of the arrows indicate the relative degrees of association and dissociation respectively.

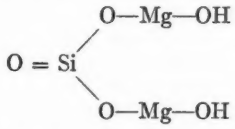
A and A' = association, a function of the nature of the ions involved.

D = dissociation or critical potential, which is greater the more highly the dissociated diffusible ions are hydrated. In the presence of electrolytes, which suppress the potential or activity of all ions, the potential of the highly multivalent colloidal ion is greatly suppressed, far below its critical value, to D'. The displaceability will then be governed by the association, for then no electrostatic attraction prevents the slightly hydrated ions from dissociating.

In connection with this anomalous behavior of Mg, we have the observations of soil geneticists concerning the accumulation of Mg in the B horizon of podzols as reported in numerous studies of Rode (18), Gemmerling and Minon (4), and Joffe (6) and the new formation of extremely stable compounds such as the polygorskite, which Poluinov (16) investigated both mineralogically and chemically and found to be composed of a hydrated Mg-aluminum silicate.

MacIntire, Shaw, and Robinson (10) describe the tenaciousness and extent of fixation of Mg in the soil complex when applied as a fertilizer to soils in the form of $MgCO_3$ and the basic carbonate in excessive amounts. They suggest that the Mg enters directly into the alumino-silicic complex.

In an attempt to contribute some light on the behavior of Mg in silicates, it was decided to start with the simple system MgO-SiO_2. Numerous studies have been made of MgO-SiO_2 complexes prepared by thermal reactions, i.e., high temperature fusions. However, a search of the literature unearthed very few papers dealing with the preparation of MgO-SiO_2 complexes in the wet way at ordinary temperatures. Jordis (7) stated that by reaction with sodium silicate solutions the alkaline earth hydroxides give metasilicates and at no time orthosilicates. Damiens (3), by mixing $MgSO_4$ and sodium silicate solutions obtained no definite compound, the composition varying from $MgO \cdot SiO_2$ to $MgO \cdot 2SiO_2$. Vournazos (19) describes the composition of a basic magnesium silicate:



formed by the extended reaction of amorphous silica and MgO at ordinary temperatures in the presence of H_2O. In none of this work was the pH in the medium considered or controlled.

EXPERIMENTAL

The initial series studied was made up by adding 0 to 64 m.e. of Mg, as as $MgCl_2$, to 19.64 m.e. of SiO_2, on the basis of $SiO_3^{=}$ from Na_2SiO_3. The series was precipitated in porcelain dishes, adjusted to disappearance of the pink color of phenolphthalein, i.e., approximately pH 8.4, allowed to stand 3 hours, adjusted to pH 8.4 again if the pink color reappeared, placed on the steam bath, and evaporated to dryness. The dried material was taken up with 50 cc. of a normal, neutral (pH 7.0) solution of NH_4Cl, the mixture was thoroughly disintegrated, allowed to stand 2 hours, and then poured through a dry filter. Twenty-five cubic centimeters of this initial filtrate was analysed for Mg and SiO_2, and a sample was taken for a pH determination. The complex was then transferred to the funnel and leached with approximately 300 cc. of normal, neutral (pH 7.0) calcium acetate, 20 cc. of $CaCl_2$, and then washed free of Cl^- with H_2O to insure removal of the excess Ca. The complex was then leached with

neutral (pH 7.0) normal NH_4Cl solution until free of Ca, as determined by NH_4-oxalate; approximately 250 cc. of NH_4Cl was used to accomplish this. The residue in the filter was then leached alternately with normal HCl and H_2O until free of Mg. The residue in the funnel was ignited, weighed, treated with HF, and found to consist of SiO_2 only. The HCl leachate was analyzed for Ca, Mg, and SiO_2, but in no case was Ca found. The NH_4Cl leachate was also analyzed for Ca, Mg, and SiO_2, after the removal of the NH_4Cl by ignition in platinum dishes. The Ca was determined by titration of its oxalate, and the Mg, as the pyrophosphate. The data are reported in table 138.

The second series was run in quadruplicate, 4 to 32 m.e. of $MgCl_2$ being added to 20.03 m.e. of SiO_2 diluted to 100 cc. in an Erlenmeyer flask. The

TABLE 138

Composition and behavior of $MgCl_2$ and Na_2SiO_3 mixtures

Mg AS $MgCl_2$*	HCl ADDED	COMPOSITION OF NH_4Cl-EXTRACT			EXCHANGEABLE				RESIDUAL		RATIO SiO_2/MgO†	
		pH	Mg	SiO_2	SiO_2	Ca	Mg	Total cations	Mg	SiO_2	Initial	Final
m.e.	*m.e.*		*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*		
0	19.79	4.6	.....	...	0.434	0.084	.....	0.084	.....	18.65	....	....
2	18.05	8.4	0.054	1.3	0.949	0.174	0.699	0.873	0.659	16.98	10.09	25.77
4	16.45	7.6	0.104	0.5	1.237	0.248	1.104	1.352	1.810	15.92	5.04	8.80
8	13.50	7.1	0.690	0.6	1.403	0.461	1.494	1.955	4.203	15.11	2.69	3.59
16	9.97	7.2	3.492	0.5	1.758	0.629	2.146	2.775	6.523	13.98	1.57	2.14
24	7.65	7.1	10.302	...	1.449	0.666	2.534	3.200	8.222	14.78	1.43	1.80
32	6.70	7.1	17.026	...	1.423	0.716	2.662	3.378	8.951	15.34	1.31	1.71
48	4.63	7.3	30.064	...	0.816	0.800	2.098	2.898	10.560	16.27	1.09	1.54
64	3.82	7.3	42.930	...	0.561	0.798	1.818	2.616	11.336	16.83	0.93	1.48

* 19.635 m.e. of SiO_2, as Na_2SiO_3, was added to each mixture.

† Initial = ratio of SiO_2/MgO in complex after 50 cc. NH_4Cl extraction.
Final = ratio of SiO_2/MgO in residual complex, after the exchange action.

pH was adjusted as before to pH 8.4; the volume in every case was made up to 150 cc.; the flasks were stoppered, allowed to stand for 24 hours with intermittent shaking, and then adjusted to pH 8.4 again if the pink color reappeared. The procedure thereafter is essentially the same as in the initial series with the exception that H_2O was used instead of NH_4Cl solution to take up the dried mixture. Also a method of successive exchanges was used, that is, at the end of the first exchange action only one funnel in each group of four was decomposed with *N* HCl, the others were subjected to a second exchange action; at the end of the second exchange action two funnels were decomposed, and the remaining funnels, one in each group, subjected to a third exchange action and then decomposition. The results are reported in tables 139 and 140.

DISCUSSION

From the data in table 138, as well as the data for the quadruplicate series (table 140), we observe that the exchangeable Ca increases steadily as the SiO_2/MgO ratio decreases. What appears to be a contradication of the results of Mattson (12) and others concerning the relation of the exchange capacity and the SiO_2/R_2O_3 ratios is due to the fact that the true SiO_2/MgO ratios are

TABLE 139

The initial composition of the Mg-SiO_2 systems

Mg added*	Number	HCl	Composition of H_2O-extract			Average SiO_2/MgO in initial complex after H_2O extraction (50 cc.)
			pH	Mg	SiO_2	
m.e.		*m.e.*		*m.e*	*m.e.*	
4	1	17.32	7.8	0.348	0.126	*5.133*
	2	17.32	8.0	0.018	0.119	
	3	17.32	8.0	0.072	0.119	
	4	17.32	8.0	0.054	0.126	
8	1	14.08	7.5	1.074	0.113	*2.787*
	2	14.08	7.5	0.822	0.113	
	3	14.08	7.5	0.786	0.080	
	4	14.08	7.6	0.726	0.086	
16	1	8.81	7.6	3.236	0.073	*1.594*
	2	8.81	7.5	3.566	0.027	
	3	8.81	7.5	3.516	0.027	
	4	8.81	7.6	3.556	0.040	
24	1	5.57	7.65	8.736	0.033	*1.268*
	2	5.57	7.65	8.020	0.020	
	3	5.57	7.4	8.194	0.033	
	4	5.57	7.6	8.000	0.027	
32	1	5.57	7.6	15.388	0.013	*1.241*
	2	5.57	7.6	16.594	0.027	
	3	5.57	7.4	15.862	0.013	
	4	5.57	7.5	15.704	0.013	

* 20.02 m.e. of SiO_2 was added to each as Na-silicate, in which the ratio of $Na_2O:SiO_2$ was 1:1.

obscured by the presence of free silica. The excessively high SiO_2/MgO ratios in the first portion of the series, however, indicate that we do not have a single complex but rather a mixture of the Mg-silicate complex with precipitated silica gel. Therefore, if the minimum SiO_2/MgO ratio (table 140) is assumed to be the composition of the Mg-silicate complex which was formed in each member of the series, it should be possible to calculate the separate ex-

change capacities of the Mg-silicate complex and of the free silica present, by means of a set of simultaneous equations of the form $Ax + By = C$, where

A = millimoles (mlm.) of $MgO\text{-}SiO_2$ complex calculated from the m.e. of the Mg in the residual mixture (values found in table 141).

B = m.e. of free SiO_2 calculated from the difference of SiO_2 in $MgO\text{-}SiO_2$ complex and the total SiO_2 in the residual mixture (values found in table 141).

x = m.e. of exchangeable Ca per mlm. of the $MgO\text{-}SiO_2$ complex.

TABLE 140

The exchangeable ions in Mg-silicate complex

	EXCHANGEABLE Ca	DISPLACEABLE Mg	DISPLACEABLE SiO_2	SiO_2/MgO RATIO AT END OF EXCHANGE‡
1st exchange (average of four funnels)				
	m.e.	*m.e.*	*m.e.*	
4*	0.226	1.004	0.903	7.692
8	0.388	1.294	1.059†	3.610
16	0.744	1.559	0.922	1.862
24	0.933	1.950	1.001	1.565
32	0.985	1.994	0.982	1.548
2nd exchange (average of three funnels)				
4	0.153	0.531	0.689	14.272
8	0.293	0.940	0.918	4.695
16	0.677	1.113	0.921	1.946
24	0.726	1.176	0.851	1.747
32	0.785	1.202	0.939	1.711
3rd exchange				
4	0.096	0.256	0.498	30.030
8	0.219	0.571	0.670	5.917
16	0.479	0.875	0.823	2.037
24	0.608	0.920	0.852	1.751
32	0.598	1.047	0.925	1.730

* Numbers correspond to the systems indicated in first column, table 139.

† Average of two funnels.

‡ These do not represent the true SiO_2/MgO ratios, for there is free SiO_2 present.

y = m.e. of exchangeable Ca per m.e. of the free SiO_2.

C = total m.e. of exchangeable Ca (values in table 140).

A typical example of the application of the method of simultaneous equations to the data obtained during the first exchange action follows:

Using the pairs of values for the 8 and 16 m.e. series from table 141 and the corresponding values of the exchangeable Ca for the first exchange action from table 140 we have:

$$2.313x + 9.487y = 0.388 \qquad (A)$$
$$4.635x + 2.764y = 0.744 \qquad (B)$$

TABLE 141

The relation of the exchange capacities to the true SiO_2/MgO ratios*

1st exchange Compn. of complex assumed for nos. 4, 8, 16, 24 = $(SiO_2)_{1.866}\cdot MgO$ Compn. of complex assumed for no. 32 = $(SiO_2)_{1.848}\cdot MgO$					
Series number†	4	8	16	24	32
m.e. Mg present‡	2.252	4.626	9.271	11.735	12.055
m.e. SiO_2 present‡	17.273	16.726	17.273	18.638	18.67
mlm. of Mg complex§	1.126	2.313	4.635	5.867	6.027
m.e. free SiO_2‖	13.749	9.487	2.764	.....	.....

Series number	*A*	*B*	*x***	*y*
4	1.126	13.749	.....	.....
			0.152	0.0040
8	2.313	9.487	0.170	0.0025
			0.160	0.0020
16	4.635	2.764	.....	.....
24	5.867	.....	0.159	.....
32	6.027	.....	0.163	.....

2nd exchange Compn. of complex assumed for nos. 4, 8, 16, 24 = $(SiO_2)_{1.747}\cdot MgO$ Compn. of complex assumed for no. 32 = $(SiO_2)_{1.711}\cdot MgO$					
	4	8	16	24	32
m.e. Mg present‡	1.065	3.007	7.141	8.718	8.628
m.e. SiO_2 present‡	15.073	14.087	13.880	15.220	14.765
mlm. of Mg complex§	0.532	1.503	3.570	4.359	4.314
m.e. free SiO_2‖	13.212	8.834	1.405	.....	.....

Series number	*A*	*B*	*x*	*y*
4	0.532	13.212	.....	.....
			0.165	0.0049
8	1.503	8.834	0.187	0.0040
			0.189	0.0010
16	3.570	1.405	.....	.....
24	4.359	.....	0.167	.....
32	4.314	.....	0.182	.....

Compn. of complex assumed for nos. 4, 8, 16, 24 = $(SiO_2)_{1.781}\cdot MgO$ Compn. of complex assumed for no. 32 = $(SiO_2)_{1.730}\cdot MgO$					
	4	8	16	24	32
m.e. Mg present‡	0.402	1.904	5.470	7.299	7.148
m.e. SiO_2 present‡	12.073	11.296	11.134	12.773	12.364
mlm. of Mg complex§	0.201	0.952	2.735	3.649	3.574
m.e. free SiO_2‖	11.370	7.962	1.557	.....	.....

Series number	*A*	*B*	*x*	*y*
4	0.201	11.370	.....	.....
			0.189	0.0050
8	0.952	7.962	0.174	0.0054
			0.171	0.0070
16	2.735	1.557	.....	.....
24	3.649	.....	0.167	.....
32	3.574	.....	0.167	.....

* After correcting for the free SiO_2.

† Nos. 4, 8, 16, 24, and 32 indicate m.e. of Mg added in making up the complex.

‡ As found by analyzing the residual complex after the exchange action.

§ Calculated on the basis of the m.e. of Mg in the complex, designated as *A* in the lower tables.

‖ Difference (designated as *B* in the lower tables) between the total m.e. of SiO_2 present and the m.e. of SiO_2 combined with Mg, the latter SiO_2 being = to the product of the "true" SiO_2/MgO ratio assumed and the m.e. of Mg complex present.

** *x* and *y*—the exchange capacities in m.e. per mlm. of Mg-complex and per m.e. of free SiO_2 respectively as calculated from the linear equations.

Solving these equations simultaneously for y, we get:

$$\begin{aligned} 10.721x + 43.972y &= 1.798 \\ 10.721x + 6.393y &= 1.721 \\ \hline 37.579y &= 0.077 \\ y &= 0.0020 \text{ m.e.} \end{aligned}$$

Substituting this value of y in equation (A) we get $x = 0.160$ m.e.

The values of x for the last two members of each series was obtained by dividing the m.e. of exchangeable Ca by the millimoles of the complex present, since free silica was assumed to be absent. Thus for series 24 during the first exchange we have:

$$x = \frac{0.933}{5.867} = 0.159 \text{ m.e.}$$

TABLE 142

Loss of the complex during exchange procedure

Mg added*	Loss of MgO			Loss of SiO_2			Ratio SiO_2 : MgO lost lost		
	I†	II	III	I	II	III	I	II	III
m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.			
4	1.625	1.187	0.663	2.624	2.200	3.000	1.615	1.853	4.525
8	2.522	1.619	1.103	3.193	2.639	2.791	1.266	1.630	2.530
16	3.260	2.130	1.671	2.705	3.393	2.746	0.830	1.593	1.643
24	4.027	3.017	1.419	1.624	3.148	2.447	0.403	1.043	1.724
32	4.058	3.427	1.480	1.333	3.905	2.401	0.328	1.139	1.622

* 20.02 m.e. SiO_2 added to each mixture (m.e. on basis of $SiO_3^{=}$).

† I, II, and III indicate the respective data during the first, second, and third exchange actions.

At the same time one can now readily see in the data thus tabulated in table 141 the trend of the values of x to increase as the true SiO_2/MgO ratios increase, i.e., after correcting for the free SiO_2. From the data in table 141 it is apparent that during the first exchange, with a complex having a SiO_2/MgO ratio of 1.565, there is an average exchange capacity of 0.161 m.e. (average value of x) per millimol of the complex, whereas during the second exchange, with a complex having a SiO_2/MgO ratio of 1.747, there is an average exchange capacity of 0.180 m.e. per millimol of the Mg complex.

The agreement in the values of x and y is very good, and it is significant that the calculated exchange capacity of the free silica is of the same order of magnitude as the value of 0.0048 m.e. per m.e. of SiO_2 obtained directly, from the data in table 138, from the sample to which no magnesium was added.

Inasmuch as the exchange capacity of the silica is low, the linear nature of the foregoing equation should become evident by plotting the exchangeable Ca

against the mlm. of the Mg-silicate complex present. Figure 40 shows a strikingly close adherence to the linearity of the function.

A similar analysis, i.e., application of the method of simultaneous equations with base-exchange data correlated with pH measurements, should enable one

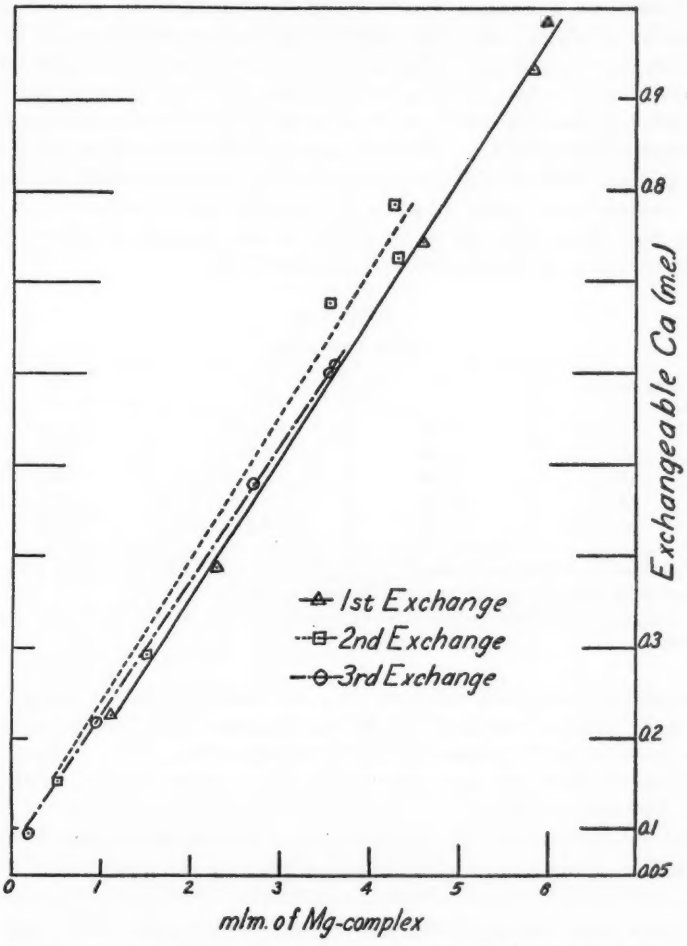


FIG. 40. THE LINEAR RELATIONSHIP BETWEEN THE EXCHANGEABLE Ca AND THE MILLIMOLS OF Mg-SILICATE COMPLEX PRESENT

to distinguish the supposedly different ferric silicates obtained by Ray and Ganguly (17) in their studies of Na-silicate solutions.

The presence of the Mg and the SiO_2 in the exchange leachate indicates that appreciable hydrolysis of the complex had taken place. In order to approxi-

mate the relative ease of hydrolysis of the complex in each group, the ratio of the total Mg lost during the exchange action to the arithmetical mean of the Mg present at the beginning and at the end of the exchange action was calculated. The ratios (table 143) indicate that the free silica present in the lower members of the series apparently has a mobilizing action upon the Mg. A similar mobilizing action was observed by Mattson and Hester (14) in the $Al.SiO_2$ system. The loss of Mg in such relatively excessive amounts during the leaching procedures is undoubtedly in great measure due to the fact that the pH of the leaching agents was 7.0, whereas the compound precipitated was the form stable at pH 8.4. Therefore, an acid hydrolysis would result during the leaching, which should result in a continuous reversion toward the form of the complex more stable at pH 7.0. Precisely this is indicated by the SiO_2/MgO ratios (table 140) of the 24 and 32 m.e. systems, as well as by the hydrolytic ratios of the same two systems (table 143).

TABLE 143

*"Hydrolytic" ratios**

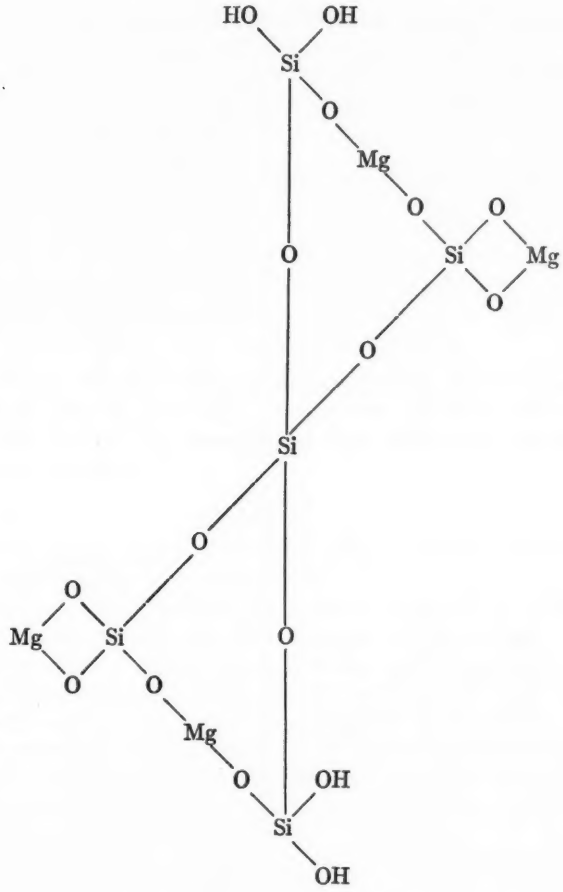
SERIES NUMBER	I†	II	III
4	0.530	0.716	0.905
8	0.428	0.424	0.449
16	0.299	0.260	0.265
24	0.293	0.295	0.177
32	0.288	0.331	0.188

* Ratio of m.e. of Mg lost during the exchange action to the arithmetical mean of the Mg present at the beginning and at the end of the exchange action.

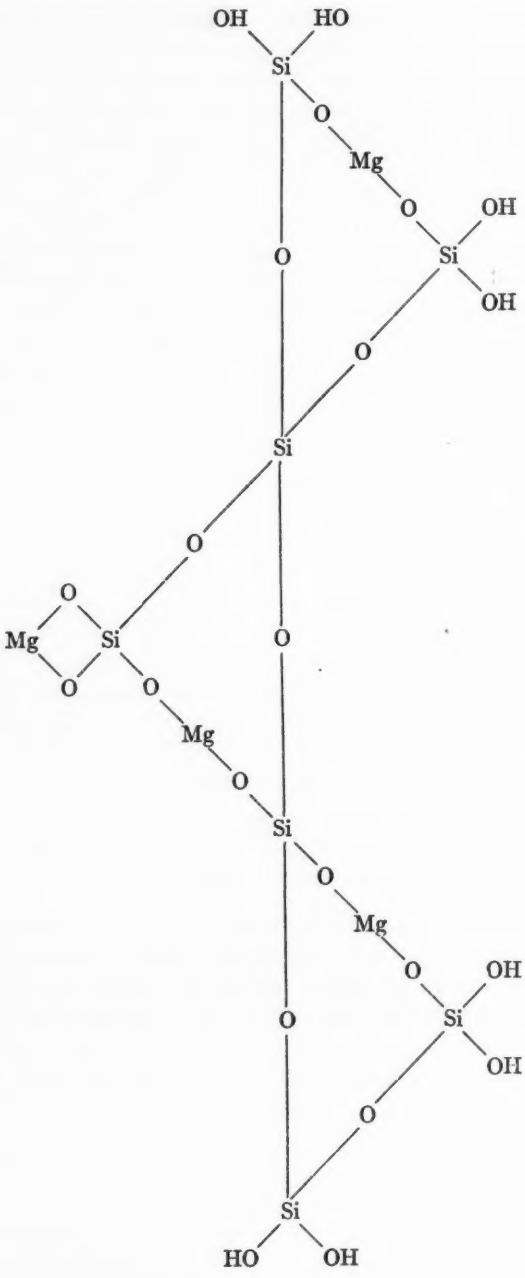
† I, II, and III indicate the respective data during the first, second, and third exchange actions.

MacIntire, Shaw, and Robinson (10), in a somewhat similar manner, explain the continued exchange of Mg and the concomitant disruption of the alumino-silicic acid complex during the determination of the exchangeable bases of soil which was previously treated with excessive amounts of $MgCO_3$ and Mg basic carbonates.

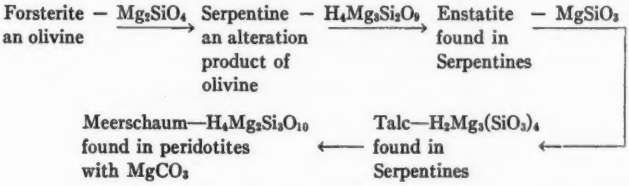
It is evident from the data in tables 139 and 140 that the compound formed by the interaction of $MgCl_2$ and Na_2SiO_3 at pH 8.4 is not stoichiometrically of the form known as the metasilicate, i.e., $MgSiO_3$. The composition indicates, rather, a higher silica content, a SiO_2/MgO ratio of 1.25, which might be pictured as follows, indicating the locking of the Mg within the complex:



As the complex was leached with a reagent at pH 7.0, according to the principles of isoelectric weathering we should obtain a compound of higher SiO_2/MgO ratio. The compound present after three successive exchange actions, having a SiO_2/MgO ratio of 1.75, could be represented as follows:


OH
HO
Si
O
Mg
O
OH
Si
OH
O
O
Si
O
O
Mg
Si
O
O
O
Mg
O
Si
O
Mg
O
OH
Si
OH
O
O
Si
HO
OH

In the 24 and 32 m.e. samples a comparison of the ratios SiO_2 lost/MgO lost (table 142) during the exchange procedure with the SiO_2/MgO ratios of the residual complex (table 140) indicates a sort of isoelectric hydrolysis which finds a singularly similar counterpart in the MgO-SiO_2 minerals found in nature, e.g., we have the series of minerals:



each one of which could be derived from the preceding mineral by a process of isoelectric weathering involving acid hydrolysis. It would be extremely interesting to investigate the association of these various minerals with each other from this viewpoint.

SUMMARY

The theories concerning the "anomalous" behavior of Mg in electrodialysis and base-exchange phenomena are discussed.

The procedure employed permitted a study of the isoelectric hydrolysis of Mg-silicate mixtures together with base exchange determinations.

Mixtures containing free silica, together with the Mg-silicate complex, yielded to a mathematical interpretation whereby the individual exchange capacities of the free silica and the Mg-silicate complexes could be determined.

It is pointed out that the mechanism of isoelectric hydrolysis is capable of accounting for various Mg-silicate minerals found in natural deposits.

Several formulas are suggested to illustrate the composition of the Mg-silicate complex at pH 8.4 and pH 7.0.

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